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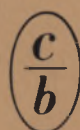
September, 1989

LITHOLOGY AND MINERAL RESOURCES

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A translation of *Litologiya i Poleznye Iskopaemye*

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The Russian press date (podpisano k pechaty) of this issue was 1/6/1989. Publication therefore did not occur prior to this date, but must be assumed to have taken place reasonably soon thereafter.

MIGRATION OF PETROGENIC ELEMENTS IN ZEOLITE
FORMATION IN ICELANDIC BASALTS

A. R. Geptner and G. V. Sokolova

UDC 550.4:552.323.5(417)

Features of the dispersal and chemical composition of zeolites in Miocene and Pliocene plateau basalts are examined. We show that it is possible to distinguish two types of mineral complexes: 1) those which form as a result of the effects on the rocks of slightly moving water, heated in the regional heat flow, and 2) those which arise from strongly heated waters actively circulating in fracture zones which transport a series of petrogenic elements over great distance.

Zeolites are very widely developed in the basalts of Iceland. This is one of the main and characteristic components of the zone of regional hydrothermal metamorphism which encompasses a thick sequence of rocks of various age and which characterizes the upper part of the altered rocks belonging to the zeolite or smectite facies [10]. Iceland is primarily made up of volcanic sequences, including a small quantity of volcanoterrigenous deposits of various genesis (marine, deltaic, lake, alluvial). Basalts predominate among the volcanites, and acid and intermediate rocks play a subordinate role. The fraction of truly acid rocks reaches from 4 to 8% in the estimates of various investigators for Pleistocene deposits [12, 13], but there is a basis for the assumption that it turns out to be even less in Miocene-Pliocene parts of section. Acid rocks occur in every territory of the island, but the greatest part of them is correlated to the large structures of the central volcanoes.

Calcic and calc-sodic zeolites (chabazite, thomsonite, mesolite, scolecite, stilbite, heulandite, laumontite) are most widely distributed in the island's basaltic sequences. Sodic types of zeolites often occur (analcite, natrolite), seldom containing potassium (phillipsite). It is established that zeolites are regularly distributed in the section of basaltic sequences. The following succession of mineral associations was detected in the composition of the predominant zeolites in Eastern Iceland (downwards): chabazite, analcite and mesolite-scolecite [14]. These are flat lying zones in section, intersecting the monocline of plateau basalts.

The succession of one zeolite association after another in the section is explained by the effect of the geothermal gradient as a result of the burial depth of the lava sequences. It was later established that below the mesolite-scolecite association it is possible to distinguish an independent association of stilbite, changing downwards to a thick laumontite zone. Approximate temperature intervals for the formation of various types of zeolites have been established [5] (Table 1). In agreement with the data of G. Walker [14], the surrounding rocks have a large influence on the composition of the forming zeolites. He connects the formation of highly siliceous zeolites principally to the transformation of nonolivine tholeiites, while high aluminum zeolites are connected to alteration of olivine basalts, which are distinguished by a decrease in silicon content. This point of view, which is widespread in the literature, does not allow for the possibility of migration of petrogenic elements from heated underground waters, and thereby assumes an isochemical process of hydrothermal basalt alteration. Until recently there was very little data on the chemical composition of the secondary minerals in Icelandic basalts, and therefore the question on the sources of the petrogenic components of zeolites and the influence of the surrounding rocks on their compositions could not have been decided unambiguously. The purpose of this article is to stress the great importance of the redistribution of a series of petrogenic elements by heated underground waters, and to show the reflection of this process in the character of zeolite distribution and features of zeolite composition.

Geological Institute, Academy of Sciences of the USSR, Moscow. Translated from *Litologiya i Poleznye Iskopaemye*, No. 1, pp. 3-14, January-February, 1989. Original article submitted February 10, 1988.

TABLE 1. Distribution of Secondary Minerals in the Zone of High Temperature Alteration of Basalts*

Alteration zone, $\sim T$, °C	Mineral indicators	Characteristic mineral complexes	Zone of zeolitization, $\sim T$, °C	Regional metamorphic facies
I 50	Smectites zeolites	Zeolites (chabazite, mesolite, scolecite, gismondite, thomsonite, stilbite, heulandite, epistilbite, mordenite, analcite, levyne), smectite, celadonite, opal, quartz, calcite, apophyllite, gyrolite	Chabazite — 70 —	zeolite facies
100			Mesolite-scolecite — 90 —	
150			Stilbite — 110 — Laumontite	
II 200	Mixed-layered smectite-chlorite	Interlayered smectite-chlorite minerals, expanding chlorites, prehnite		
III 250	Chlorite-epidote	Chlorite, epidote, prehnite, albite (in volcanic glass, in interstices, in plagioclases), sphene, potassium feldspar		
IV 300	Chlorite actinolite	Chlorite, albite, actinolite		Greenschist facies

* Compiled from [4, 5, 10], with supplements from A. R. Geptner.

Features of the Distribution of Secondary Minerals in the Zone of Zeolitization. Zonal distribution of secondary minerals in the sequence of the Miocene plateau basalts of Iceland was first shown by G. Walker [14]. The zonality is most distinctly expressed in the zeolite distribution. In succeeding years an analogous distribution of zeolites in Miocene and younger vulcanites was also established in other regions of the island [7-11].

Study of the distribution features of secondary minerals in lavas, various forms of volcanoclastites, and the volcanoterrigenous deposits interlayering with them, showed that the intensity of the transformation of rocks with varied composition and genesis depends primarily on the permeability and on the duration of the interaction with underground waters. In the process of hydrothermal metamorphism of lavas, dikes, and various volcanoclastites, the permeability noticeably decreases as a result of the partial or complete filling of pore space by mineral components. Prolonged and intensive interaction of rocks with underground water is better provided where constant renewal of the fracture system occurs. Thus, for example, it is established that in the plateau basalt sequence, the rocks were most intensely altered in zones of faults and fracture swarms. Beyond the limits of these zones in lavas buried by more than 1 km, weakly altered rocks are widely distributed, and rocks may occur which are completely deprived of secondary minerals.

Two methods of formation are distinguished among the secondary components of the zeolitization zone: metasomatic minerals and minerals synthesized from solutions, or minerals forming by recrystallization of gels. In sequences with varying degrees of alteration, the relation of the primary rock components and the metasomatic and synthesized secondary minerals have the following general form. In rocks with unaltered primary minerals, secondary components occur in the gas cavities of lavas, and in the fractures of intergrain space of tuffs, various hyaloclastites, and volcanoterrigenous rocks. The similar relation indicates that the secondary minerals were synthesized from solutions, which were moving in the pore space of the rocks. In rocks with weakly altered primary minerals, the partial or complete replacement of olivine is observed, while plagioclases are replaced only along fractures, and the formation of palagonite is observed on the edge zone of fragments of sideromelane glass. Secondary minerals synthesized from solutions are distributed in gas cavities of lavas, in the intergrain space of volcanoclastites and volcanoterrigenous rocks, and by fractures. Strongly altered rocks are distinguished by the fact that in them sideromelane and the more acid remnant glass of lavas, as well as olivine, are completely replaced by secondary minerals. Plagioclases are partially or completely altered, while pyroxenes are mainly unaltered. Every pore space is filled by a complex of secondary minerals.

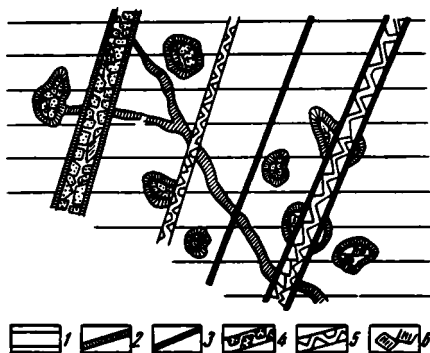


Fig. 1. Relation of various aged mineral associations: 1) basalts of lava flow; 2) smectite; 3) celadonite; 4) zeolite; 5) quartz; 6) calcite.

In the zeolite zone, propylitization zones are distributed beyond the limits of high temperature processing of rocks by ascending flows of waters; the existence of a definite succession of secondary mineral formation is established, which stands without alteration in sequences of great thickness and extent. The most widely distributed association is that of formation of clay minerals first (smectites, celadonite, or chlorite), and then zeolites with siliceous minerals (opal, chalcedony, quartz). Significantly less often a mineral association occurs with an inverse succession, when siliceous minerals or zeolites occur earliest, and clay minerals formed in the latter stages of secondary mineral formation in the given volume of rock. In a few cases segregation of zeolites not accompanied by clay minerals was successfully observed. Smectites and celadonite associate with low temperature zeolites, while chlorites, as a rule, occur at high temperature levels in the laumontite zone.

The wide development of stratiform separations in the above-noted mineral association is extremely characteristic of the regional hydrothermal metamorphism of the zone of zeolitization. In microscopic cavities of various forms and occurrences (gas cavities in lavas, intergrain space of volcanoclasts, fractures) and in coarse spaces of rocks, it is very often possible to observe frequent alternation of subparallel layers of smectites, zeolites, opal, and/or chalcedony or complex aggregates of these minerals. In conditions of well exposed stratiform separations, the interlayers could reach hundreds of meters. In young, tectonically undisturbed sequences, the stratiform separations are always horizontal. Monoclinally lying sequences of Miocene-Pliocene plateau basalts are intersected by horizontally arranged levels of secondary mineralization. This fact, in the same way as in the above-noted level-lying zeolite zones [14], uniquely attests to the later, superposed character of the smectite-zeolite mineralization. The similar distribution of secondary mineral points to the transformation of basaltic sequences by heated underground waters of layer-fractured circulation. The widely distributed stratiform separations of secondary minerals in the limits of fracture swarms also serve as corroboration.

Numerous signs exist of the multiple formation of fractures and alteration of the composition of secondary minerals in fractures of different generations. It is possible to consider the Miocene plateau basalts of Eiyafjord (Northern Iceland) as an example of the interrelation of mineral associations with different composition in gas cavities and the fractures cutting the lava sheets. Here a sequence of monoclinally lying plateau basalts is split by numerous fractures grouped in several variously directed systems. The primary fracture system, which cuts the plateau basalts transverse to strike, was apparently the most long lived. It is distinguished by the greatest variety of combinations of clay minerals, zeolites, siliceous minerals and calcite. Figure 1 shows a fragment of a vesicular lava sheet split by a system of mineralized fractures with a northern trend. Veins of secondary minerals cut several flows. Secondary minerals of the gas cavities include (in order of formation): celadonite, smectites, zeolites, quartz (sometimes chalcedony), and calcite. Smectites are arranged in the form of rims of different sequences on the cavity walls. Calcite generally fills the space remaining free between crystals of zeolites and quartz. In the intersecting veins celadonite occurs very seldom, smectites form fine rims in them, and zeolites and quartz (or chalcedony) play the major roles. In several fractures filled by zeolites and quartz, clay minerals are not detected. In particularly coarse, open fractures cutting the lava flows, the selections of the zeolites have the form of cylinders overlapping one another, indicating the growth of crystalline aggregates from a solution moving downwards along the fractures. For fractures with displacement it is established that tectonic motion in this region

TABLE 2. Change in the Composition of Zeolites from Fracture Swarms

Hypsometric position, m	Si/Al		
	chabazite	stilbite	heulandite
600	-	2.65	-
350	1.87	-	-
300	2.15	-	-
270	2.00	-	-
230	-	3.36	-
170	1.89-1.86	-	-
130	-	3.44	-
80	2.34	-	-
40	1.85-2.11	2.46	3.77
5	-	3.89	-
0	-	3.07	2.56
-76	-	-	3.54-2.81
-78	-	-	3.29
-576	-	2.66	-

occurred simultaneously with the formation of secondary minerals, and after it. Thus, for example, in the crush zone of a small fault (zone width 0.5-1.0 m, amplitude of displacement 10-12 m), the breccia is cemented by zeolites, and displacement deforming zeolite crystals inside the veins was successfully recorded. The indicated features of basalt mineralization show that fractures once clogged by secondary minerals were then repeatedly renewed and filled by new portions of underground waters. At the same time, the composition of the underground waters did not remain constant, according to the effect on the composition of the forming secondary minerals. The cited stratiform alternation of mineral associations in the basalts attests to the multiple character of the change in the underground water compositions. It is very important to stress that secondary minerals, including zeolites, are distributed not only in the plateau basalts, but also in the dikes breaking them. As in the layer basalts, there is overlapping of mineralization in the dikes, and consequently the dikes could not be considered as a synchronous source of heat for the formation of heated underground waters.

Relation of the Composition of the Zeolites and the Surrounding Rocks. In considering the relations of the composition of the zeolites and the surrounding rocks, it is necessary to take into account that in many cases two or three, and sometimes a greater number of mineral forms are present in the rocks of a single occurrence. Zeolites of various forms, filling spaces, are generally found in close intergrowth. It does not seem possible to divide them mechanically, and therefore the data of chemical and x-ray analyses are obtained for aggregates of several mineral forms for very many samples. Optical and electron-microscopic investigations were of great help in deciphering the formation conditions of newly forming minerals, which made it possible in a series of cases to establish a succession for the formation of zeolites of various form.

In Northern Iceland, in the Eiyafjordur region, in a monoclinally lying sequence of Miocene plateau basalts, chabazite, analcite, mesolite-scolecite, stilbite, and laumontite zones of zeolitization are arranged downwards, encompassing a section nearly 3 km in thickness [5, 10]. The upper part of this section in the Loigaland region is primarily represented by olivine basalts with separate marker horizons of plagiophyric basalts which also contain olivine. The basalts are cut by thick dike swarms of northern strike, the width of which at the apex of the fjord reaches 10 km. In this direction, the basalts are cut by numerous fractures, forming swarms, the width of which is greater than the dike swarms. Vertical movements up to several tens of meters in amplitude occurred in several discontinuous disruptions. Combined swarms of dikes and fractures also with northern strike cut the sequence of plateau basalts on the eastern side of the fjord and the lower part of the Fnjoskau river valley.

In the upper zeolite zone besides the most widely distributed chabazite, one may generally distinguish the presence of thomsonite, levyne, and phillipsite [5, 14]. They are apparent in the olivine-containing basalts of Eiyafjord within the limits of the fracture swarms on this level, while in several occurrences such high silicon zeolites as stilbite, heulandite, and mordenite dominate. Analcite often occurs here. Small quantities of scolecite and laumontite are detected in the composition of the mineral association on the hypsometric level of the chabazite zone. These are zeolites characteristic of intervals of hydrothermal

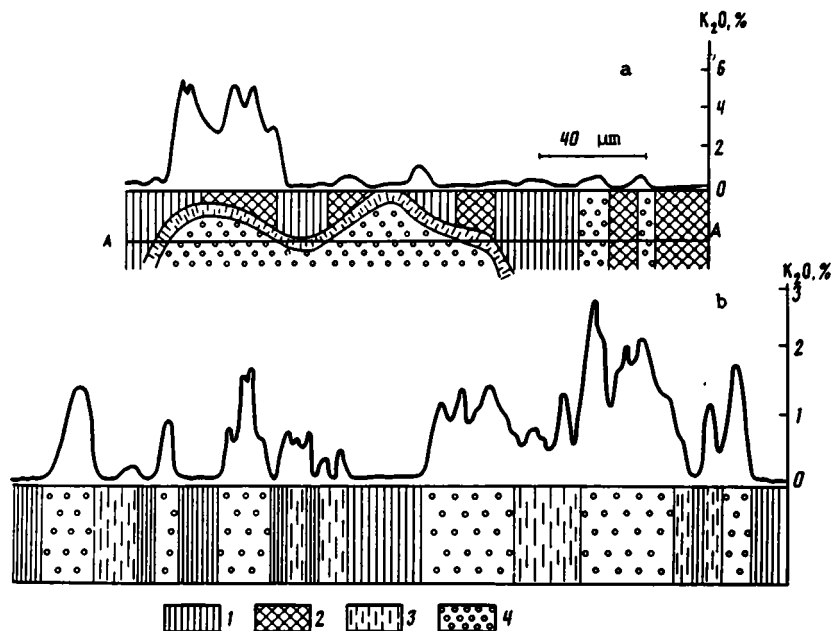


Fig. 2. Potassium distribution in zeolites and smectites, filling gas cavities (a) and fractures in plagioclase phenocrysts (b). 1) Plagioclase; 2) pyroxene; 3) smectite; 4) zeolite; AA) position of the microprobe profile.

reworking with higher temperatures. In the chabazite zone, stilbite, heulandite, and mordenite very often occur together with opal or chalcedony, while they occur with quartz in more strongly heated rocks. The following structural-temporal interrelations of zeolites are characteristic and most widespread (early-late): chabazite-stilbite, chabazite or thomsonite-analcite, stilbite-mordenite, mordenite-heulandite. In this region stilbite, mordenite, and heulandite are widely developed in section only in the mesolite-scolecite zone, while stilbite also occurs in large quantity lower, together with laumontite reaching depths greater than 2800 m below sea level in well Lj-8 [10]. Zeolites of the mesolite-scolecite and laumontite zones associate with quartz in every section, within the limits of fracture swarms. Fracture type zeolitization and silicification are widely developed here apart from pore zeolitization. High temperature zeolites are later, and are superimposed on horizontally lying zones of zeolitization. The wide development in the basalts of the association of high temperature zeolites and siliceous mineral and their transzonal distribution, which are correlated to the cutting fracture swarms, make it possible to speak confidently on the migration of the basic petrogenic components with heating of underground waters. The effect of the surrounding rocks on the composition of the zeolites forming here was extremely limited. Such a conclusion was made by investigation of the composition of zeolites, reflected at various hypsometric levels of the Eiyafjord plateau basalt sequence. The significant variation in the content of silicon and aluminum in chabazites, stilbites, and heulandites attracts attention. In agreement with zeolite classification, in the amount of Si/Al among chabazites (1.85-2.34) intermediate and high aluminum varieties exist, while among stilbites (2.46-3.89) and heulandites (2.56-3.77), there are intermediate and high silicon varieties [2]. These variations are irregularly arranged in the section of the plateau basalts (Table 2). All zeolite analyses are selected from the sequence of olivine-containing basalts far from occurrences of acid rocks. Change in the silicon and aluminum content in zeolites of one type could probably be connected with the migration of silicon into the sequence of basalts and with the change of this component's concentration in the underground waters irrespective of its dependence on the composition of the surrounding rocks. The correctness of this assumption is confirmed by the insignificant adoption of components from the rocks during alteration of sequences at the temperature level of the zeolite facies. Let us consider an actual example. A sequence of plateau basalts is exposed in the Fn'oskau river valley, which includes several horizons of acid tuffs, ignimbrites, and andesites (icelandites). The basalts and acid rocks contain various quantities of smectites and zeolites, depending on their porosity and permeability. These smectites and zeolites formed primarily from solutions. Particularly abundant deposits of zeolites are correlated to the porous

TABLE 3. Chemical Composition of Basalts from Unaltered and Hydrothermally Altered Parts of the Miocene Sequence of Plateau Basalts (Vatnsfjord, Northwestern peninsula)

Component	Sea level					Slope of Mount Isufedl', 470 m and above sea level				
	79173	79174	79175	79176	79177	79165	79167	79169	79171	79172
SiO ₂	44,77	47,03	47,38	44,43	44,78	49,40	48,11	48,13	47,88	47,45
TiO ₂	1,63	1,40	1,53	1,53	1,22	1,68	1,88	1,74	1,63	1,57
Al ₂ O ₃	15,90	18,09	17,11	14,70	15,14	15,08	16,34	16,10	16,78	16,84
Fe ₂ O ₃	1,30	3,40	1,62	6,73			2,61	2,08	0,89	2,23
					9,68*	12,97*				
FeO	9,00	4,94	7,69	3,26			8,38	8,96	9,31	7,55
MnO	0,21	0,17	0,21	0,21	0,20	0,21	0,23	0,23	0,21	0,21
MgO	7,03	6,56	7,22	6,47	6,12	7,30	6,80	7,12	7,09	7,77
CaO	12,31	12,87	12,45	11,91	11,90	12,90	12,53	12,77	13,02	13,10
Na ₂ O	2,05	1,95	2,05	1,29	1,46	2,08	2,38	2,38	2,16	2,27
K ₂ O	0,57	0,26	0,44	0,26	0,44	0,35	0,26	0,31	0,26	0,22
H ₂ O ⁺	1,25	1,37	1,17	6,69	Not	det'd	0,16	0,25	0,40	0,28
H ₂ O ⁻	0,78	1,41	0,70	2,41	"	"	0,12	0,04	0,28	0,20
P ₂ O ₅	0,16	0,41	0,16	0,15	0,16	0,19	0,17	0,16	0,15	0,16
Total	99,96	99,56	99,73	100,04	91,10	102,16	99,97	100,27	100,06	99,85

* Total iron.

parts of the flows. Two chabazite samples were investigated from lavas which directly cover thick packets of acid tuffs and ignimbrites. In their chemical composition and in particular in their Si/Al magnitude, which equalled 1.99-2.07, they proved to be close to those which formed in a homogeneous sequence of olivine-containing basalts.

The characteristic feature of zeolites collected from Miocene basalts in various regions of Iceland is the significant variation in their potassium contents. The primary concentrations of this element are found in phillipsite, mordenite, heulandite, and chabazite. Potassium containing laumontite occurs. Most often potassium-containing minerals occur in basalts, which are cut by fracture swarms. The Miocene basalts of Iceland in which secondary minerals have not been established by optical methods contain very little K₂O. The maximal value for the background content of this component may be understood to be 0.3-0.4% [1]. In basalts with secondary minerals (these are most often smectites and zeolites) the quantity of K₂O is sometimes increased up to 0.6-1.2%. In the two previously cited samples of chabazites from basalts of the Fn'oskau River much K₂O (1.35 and 2.44%) and little Na₂O (0.45%) is detected. With the exception of such cases where secondary minerals are formed in acid rocks, where potassium is quite common, during the alteration of low potassium basalts the increase of this element in comparison with background content in secondary minerals is determined to indicate its entrance with hydrothermal solutions. Potassium-containing zeolites often occur together or neighboring fracture swarms with silicic new formations. Generally this is an opal-chalcedony-celadonite-smectite association. Below is shown a comparison of the composition of this association and surrounding basalts:

	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O
Surrounding basalts	48,49	3,63	12,49	16,67	0,26	4,71	8,93	2,89
Silico-celadonite-smectite-association	83,79	0,29	3,80	3,21	0,02	0,94	1,48	0,37
	K ₂ O	P ₂ O ₅	BaO	SrO	Cr ₂ O ₃	NiO	Calc. loss	Total
Surrounding basalts	0,38	0,42	0,01	0,01	0,03	0,03	0,64	99,59
Silico-celadonite-smectite-association	1,16	0,08	0,01	0,00	0,01	0,01	0,45	99,62

Similar mineral paragenesis indicates the closeness of formation conditions, and a possibly single source for the entrance of silicon and potassium for the indicated mineral associations. An increase in the potassium content in low-alkaline basalts is noted over a distance of many tens of kilometers from the large thermal anomalies (large volcanic centers) and the zones of deep hydrothermal processing of rocks which are connected with them. The superimposed character of potassium mineralization may be shown in an example of the distribu-

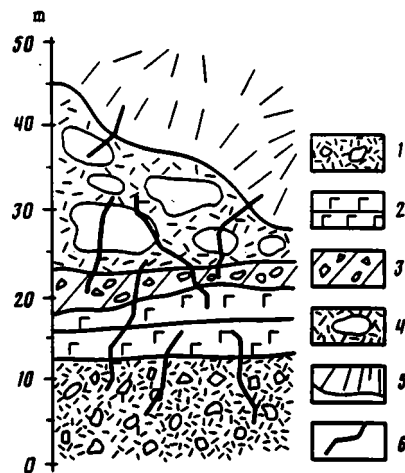


Fig. 3. Calcite-stilbite veiny mineralization in basaltic and dacitic hyaloclasts: 1) basaltic (sideromelanitic) hyaloclastites; 2) lava flows of basalts; 3) tillites; 4) dacitic hyaloclastites; 5) dacitic lavas; 6) veiny zeolites and calcites.

tion and compositional features of secondary minerals in Miocene plateau basalts from Vatnsfjörður (the Northwestern peninsula of Iceland). A monoclinally lying packet of surface lavas of basalts, traced from sea level to a height of 700 m is investigated here. Below 470 m, all of the gas voids and fractures in the lavas are filled by secondary minerals. These are primarily zeolites with smectites in small quantities. Secondary minerals do not occur above this level in a majority of the investigated samples. In single cases in rocks forming the sides of a glacial trough, opal and iron hydroxides are detected. Results of the chemical analysis of basalts taken mapped at sea level and above the absolute marker of 470 m are shown in Table 3. The altered basalts are distinguished by a high level of hydration and oxidation, a lower quantity of silicon, and doubled K_2O . Zeolites may be divided into two groups based on the character of their interrelation with the surrounding rocks: 1) those filling gas cavities and 2) those sealing fractures. The distribution of potassium in zeolites was investigated by microprobe in samples with undisturbed structures (analysis was carried out by M. A. Selezneva). Results of the investigations are shown in Fig. 2. It is first of all necessary to pay attention to the absence of potassium in the plagioclases of the source rocks. This completely agrees with data available in the literature. In the porphyritic and olivine basalts of the tholeiite series and the alkaline-olivine-basalt series of Iceland, K_2O is not detected in plagioclases, while potassium enriches the basic mass of porphyritic varieties [1]. In the fresh samples of fine grained basalt we investigated, the potassium was concentrated between the crystals of plagioclases and pyroxenes, apparently in acid glass remnants. In hydrothermally altered rocks, potassium is detected in zeolites, and the majority of it (5-11%) is found in such crystals which fill gas cavities, that is, which form from solutions. From the cited data it is seen that not all of the optically identified crystals of zeolites in the gas cavities contain much potassium, and it is nonhomogeneously distributed in the field of development of this mineral nonhomogeneously. Potassium is detected in zeolites and smectites in fractures which cut plagioclase phenocrysts. In comparison with the zeolites of gas cavities, it is much less here. The character of the distribution and the relation of the potassium content in the original rock, in the zeolites of gas cavities and fractures, does not leave any doubt on the entrance of this element into the rock primarily by underground waters. On the basis of these data it is natural to propose that it is probably necessary to consider the above-noted appearance of phillipsite in the chabazite and mesolite-scolecite zones rather as an indication on the migration of potassium into the plateau basalts sequence, not as a result of the isochemical alteration of low potassium basalts by the metamorphism of burial. Data are available showing that formation of some zeolites occurred in conditions of intense migration of Ca in basalts. On the north shore of Khvalfjörður, a portion of the section of Pliocene plateau basalts was studied that includes a thick sequence of dacite lavas and hyaloclastites, tillites, and basaltic (sideromelane) hyaloclastites (Fig. 3). On this hypsometric level, the secondary minerals of basalts are from the chabazite zone of the zeolite facies. On the studied portion of the rock the strongly altered lavas and hyaloclastites include large quantities of smectites, zeolites, and calcite. The rocks are cut by fractures, filled by calcite and zeolites. Coarse stilbite crystals were collected in one system of veins cutting the dacite hyaloclastites and lavas, as well as the underlying rocks. On the dense portions the dacites are weakly altered, while the glass is partially replaced by smectites where they are cut by a perlitic fracture system.

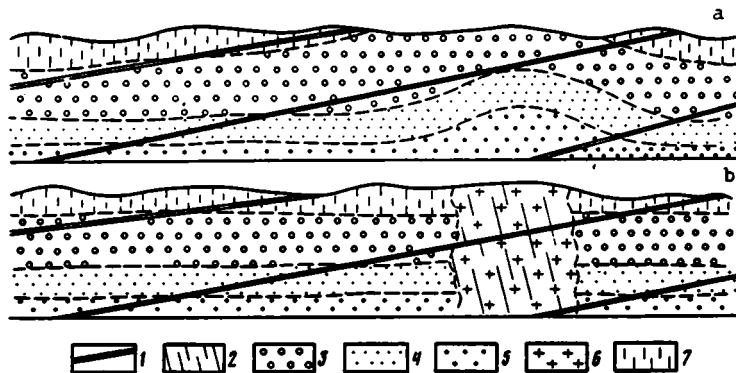


Fig. 4. Zeolitic mineralization in Miocene plateau basalts (variants of relations of different zeolization zones: a) after G. Walker [14]; b) set out in this article): 1) monoclinaly lying plateau basalts; 2) dike and fracture combined swarms; 3)-5) zeolite metamorphic zones of burial [3) chabazite, analcite; 4) mesolite-scolecite, stilbite; 5) laumontite]; 6)-7) covering zone of alteration [6) zeolite mineralization and silicification; 7) basalt without zeolites].

All of the gaping fractures and intergrain spaces of the hyaloclastites are filled by stilbite and calcite. In the basaltic lavas underlying the dacites, the gas cavities are encrusted by smectites, while the central part are filled by zeolites.

Sideromelanitic hyaloclastites are almost completely filled by smectites. The chemical composition of fresh and hydrothermally altered portions of dacite and stilbite from the fractures cutting it are shown in Table 4. As seen from presented data, the altered portions of the dacite are depleted in silicon and sodium, contain much water, and are enriched by calcium. The formation of calcite and stilbite in the fractures reflects the great activity of calcium in underground waters. It is completely probable that in the given case, a significant part of calcium entered into dacites from underground waters for formation of calcite and stilbite. Considering that the temperature intervals of stilbite formation are significantly higher than in the chabazite association [5], it is possible to propose that calcium was withdrawn from the sideromelane hyaloclastites by rising flows of strongly heated waters.

Investigation of the composition and the distribution characteristics of zeolites in the sequence of Pliocene-Miocene plateau basalts makes it possible to distinguish two types of secondary mineralization by the interaction of heated underground waters in the surrounding rocks. The first type is formed by the hydrothermal alteration of burial. In the process of accumulation and subsidence of the lava sequences below the level of underground waters heated in the regional thermal field, thick and wide sequences of basalts were altered dependent on burial depth. Increased temperatures with depth caused the appearance of zeolite zones successively replacing one another in the basalt sequence: chabasite, analcite, mesolite-scolecite, stilbite, and laumontite. The secondary minerals of these zones were formed by the active interaction of slowly circulating underground waters with the surrounding rocks. The second type of alteration is connected with strongly heated, mineralized and actively circulating waters. High temperature hydrothermal systems arose in the body of large volcanic structures of the central type approximately at the same hypsometric level as the zeolite facies. In strongly heated parts of the volcanic structures zones of propylitization, silification, and intense calcitization were formed as a result of deep alteration of basalts and acid rocks. Waters enriched by dissolved components were laterally dispersed in fracture zones far from the limits of the volcanic structures, also permeating the more ancient sequence of plateau basalts, which had been altered in the regional thermal field dependent on burial depth. The often-observed increase in the intensity of secondary mineral formation in the fracture swarms is connected with the increased permeability of the rocks and the active circulation of strongly heated waters in them. The correlation of highly siliceous and potassic zeolites to these zones, the enrichment of caltic-sodic zeolites by potassium, and their paragenetic combination with siliceous minerals make it possible to connect the entrance of silicon and calcium into the basalt sequence with underground waters from the region of central volcanic structures.

TABLE 4. Chemical Composition of Stilbite and Surrounding Rocks

Compo- nents	Massive portion of dacites	Dacitic hyaloclastites with secondary minerals	Stilbite from fractures cutting the dacites
SiO ₂	63.93	58.71	56.11
TiO ₂	0.82	0.85	0.09
Al ₂ O ₃	14.15	13.56	15.48
Fe ₂ O ₃	1.68	5.38	0.89
FeO	4.55	0.77	0.14
MnO	0.11	0.07	-
MgO	1.01	0.96	0.18
CaO	3.98	5.00	8.21
Na ₂ O	4.32	2.10	0.88
K ₂ O	1.47	1.99	0.10
H ₂ O ⁺	3.37	5.94	14.15
H ₂ O ⁻	0.63	4.50	3.28
P ₂ O ₅	0.19	0.17	-
Total	100.21	100.00	99.51

Thus, based on the investigation of the character of zeolite distribution and composition in the sequence of plateau basalts of Iceland, it is possible to distinguish two types of mineral complexes: 1) those forming as a result of action on rocks of weakly moving waters, heated in the regional thermal flow, and 2) those arising from strongly heated waters actively circulating in fracture zones which transport a series of petrogenic components over great distance. This in its turn makes it possible to otherwise interpret the interrelation and distribution of the various zeolite associations (Fig. 4). In agreement with existing assumptions, flat lying zones of zeolitization in dike swarms curve smoothly upwards. The intensity of secondary mineral development is increased here [14]. This is considered a consequence of a local temperature increase connected with the intrusion of a large quantity of dikes and contact metamorphism. In materials from deep wells drilled in Reidarfjord (Eastern Iceland) in the limits of the dike swarm, three stages of secondary mineralization are noted. They include threefold formation of laumontite [3, 9, 15]. Data obtained for the plateau basalts and the dike swarms which cut them of the Eiyafjörður region (Northern Iceland) indicate the presence of at least two stages of zeolite mineralization not connected with dike intrusion. Zeolite formation in the first stage is connected with the heating, differentiation in the section by heating of plateau basalts, and formation of the mineral associations of the flat lying zones. Zeolites of the fracture swarms include relatively more high temperature forms, arranged in a cutting position relative to the metamorphic zones of burial. The formation of the second stage minerals is connected with existence of zones of active circulation of strongly heated waters, interacting with lavas and the dikes cutting them. In this zone, the secondary mineral associations of the lavas and dikes are analogous.

The authors consider it their debt to thank the National Science Council of Iceland for making it possible to conduct field work.

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CLAY MINERALS IN DEEP WATER HYDROTHERMAL STRUCTURES OF THE GUAYAMAS DEPRESSION (GULF OF CALIFORNIA)

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We discuss results of the study of clay formations from the compositionally complex hydrothermal, substantially sulfide structures developed on the floor of the rift trough in the Gulf of California. The clay material comprises thread-like-paniculate and dendritic aggregates. It is represented by hydrated talc, expanding talc, and saponite. We compute the mineral formulas, and consider questions on the mechanism and formation conditions of the encountered mineral forms.

In recent decades, several regions with development of active thermal sources depositing sulfide ores have been detected in the eastern part of the Pacific ocean. Almost every region of hydrothermal activity here has been correlated to the rift of the East-Pacific system of spreading ridges. The sources are arranged at a significant depth, and at their outputs they create structures of complex mineral composition, with varying quantity and form: mounds, cones, needles, tubes, towers. Sometimes they are called "thermites" or "smokers" due to the "smokes" observed above them, which represent clouds of suspended material. Black and white smokers are distinguished, dependent on the character of the suspended material: ore components predominate in the first (mainly pyrrhotite), and nonore in the second (sulfates, carbonates, and silicon).

The discovery of an underwater hydrothermal ore accumulation forming "under our eyes" attracted great attention from geologists, and regions of mid-ocean ridges began to be intensely studied with the goal of both comprehensive study of oceanic ore formation processes, and also of searches for new ore fields. The utilization of underwater manned apparatuses assisted the effectiveness of the investigators.

Geological Institute, Academy of Sciences of the USSR, Moscow. Translated from *Litologiya i Poleznye Iskopaemye*, No. 1, pp. 15-22, January-February, 1989. Original article submitted May 16, 1988.

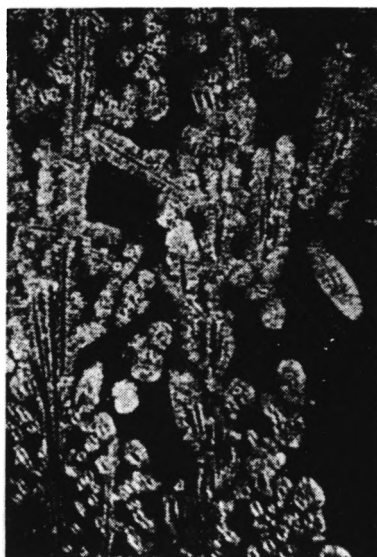


Fig. 1

Fig. 1. Fibers formed of fine lamellae of saponite (sample 1529-3). Thin section, with analyzer; $\times 35$.

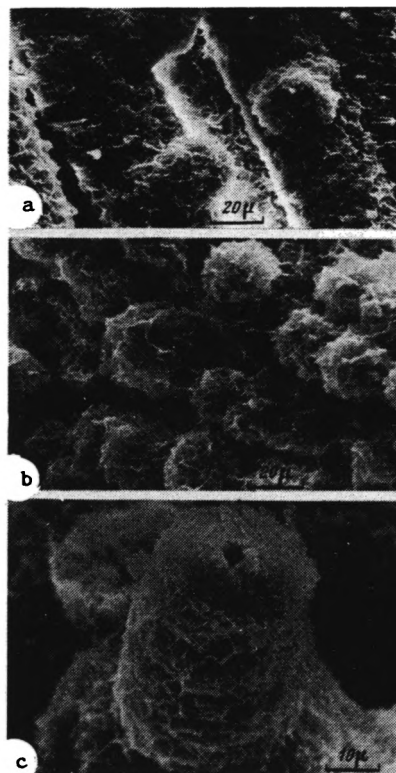


Fig. 2

Fig. 2. Microstructures of clay aggregates (sample 1541): a) particle from solid clay lamellae; b) clay lepispheres with space in the nucleus from a dissolved crystal.

An appropriate expedition was organized in 1986 by the Institute of Oceanology of the Academy of Sciences of the USSR (NIS "Akademik Mstislav Keldysh," 12th voyage). It was headed by chl.-kor USSR Academy of Sciences A. P. Lisitsyn. One of the work areas was located in the Gulf of California in the Guayamas trough, where American investigators had earlier detected hydrothermal activity.

As is known, numerous young spreading centers (rifts) occur along the gulf. They are morphologically expressed as troughs; the latter are complicated by small fractures and are divided by lengthy transform fault-shears with northwest strike. Two troughs arranged in linked-shape are correlated to the Guayamas trough. High temperature anomalies are connected with them. Wells were drilled in the troughs: number 477 in the southern trough and 481 in the northern; the first is located just within the limits of such an anomaly. Neither well reached basement. Features of the California rift system are a generally high sedimentation rate (up to 2700 m/million years) and the absence of basaltic extrusion products on the rift floor (trough). At the same time, doleritic dikes and sills of late Quaternary age, including thick examples, occur in the sedimentary sequence opened by wells. In well 477 one spans the interval 58-105 m.

Material forming the base of our investigations was collected during the above mentioned expedition to the hydrothermal field in the southern trough. The expedition obtained great and varied information on the formation of ore and nonore hydrothermal accumulations. We note that in earlier published articles, primary consideration was given to the material-mineralogical characteristics of the ore components, and fewer data were presented on the composition and particularly on the structure of the nonore components, although the latter are a significant, and sometimes major part, of the hydrothermal formations. They are polymineralic, and represented by barite, Ca sulfates (gypsum, anhydrite) and carbonates (calcite), quartz, opal, and clay minerals, composed of structurally complex combinations both among themselves and with metallic components.

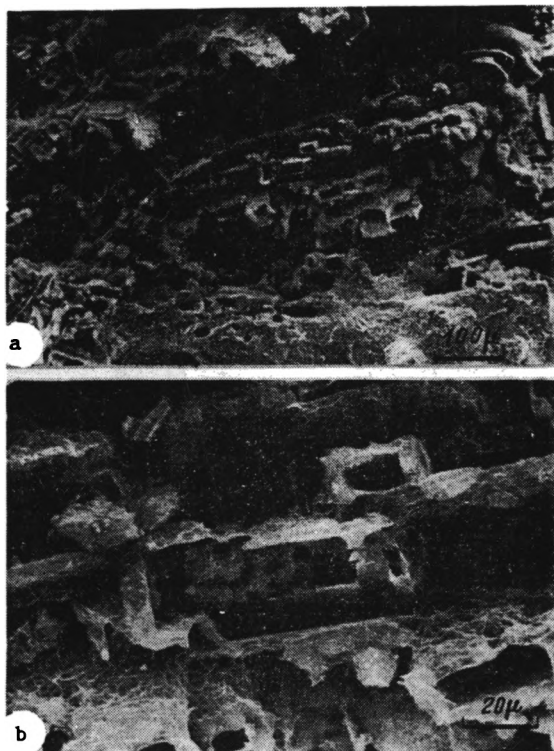


Fig. 3

Fig. 3. Microstructures of clay aggregates (sample 1541). Clay "cassings" on crystallomorphic spaces.

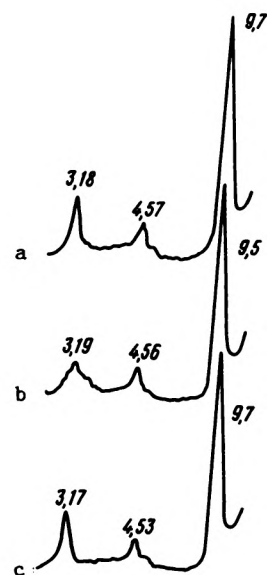


Fig. 4

Fig. 4. Diffractograms of sample 1541, obtained from specimens a) air-dry; b) saturated in ethylene glycol; c) fired at 550°C.

In this article we only present results from the study of the clay formations. We will analyze in detail five characteristic samples (1519, 1541, 1583/4, and 1614a, b)* from four hydrothermal structures with heights of 5 (two), 7, and 45 m, the base of which is located on the trough floor at a depth of nearly 2 km. Four samples are related to small "parasitic" structures, complicating the slopes and bases of larger. Sample 1541 was taken close to an active vent, the temperature of which reached +100°C. Sample 1519 was also situated adjacent to a source, while the ground is strongly saturated by liquid bitumen at this point.

Outer Form and Structure of Clay Formations. This is a light, porous-vesicular, very brittle rock of uneven light and dark grey color. With the naked eye it is apparent that it is composed from variously oriented fine fibers, comprising fanlike and paniculate aggregates. By consideration of samples under a binocular magnifying glass, it is sometimes quite apparent that fibers were grown around by dendritic-appearing outgrowths (sample 1583). Fine rosettes of gypsum and drusey calcite are locally observed in vesicles. Sulfide crystals are scattered in many sections of the rock, sometimes abundantly.

Microscopic study of transparent thin sections showed that the basic rock component is very fine recrystallized clay material. It is generally comprised of straight and bent fibers with thickness from 0.02 to 0.15 mm (Fig. 1). Their interior part is often hollow, while the faceting of the spaces indicates that there were lamellar crystals and their intergrowths here. Some of the latter resemble organogenic remnants in form. The clay mineral lamellae are generally arranged perpendicular to the surface of the fibers, and they comprise a series of ultrafine zones distinguished by various recrystallizations of material. The more such zones, then the thicker the fibers. Their surface is often covered by hemispheres or branches of the same material. Details of structure are well revealed by electron microscopic investigation of samples. The clay minerals are formed by curved book-

*Samples were raised by underwater routes by M. I. Kuz'min, A. P. Lisitsyn, Yu. A. Bordanov, and L. I. Moskaev.

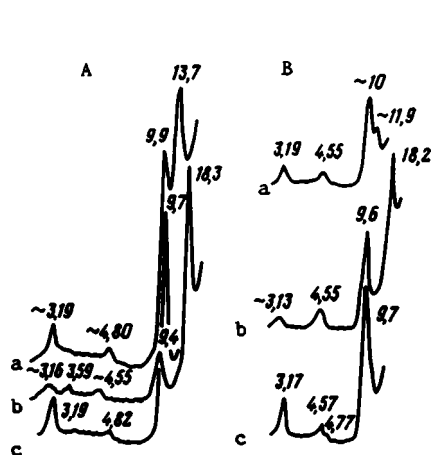


Fig. 5

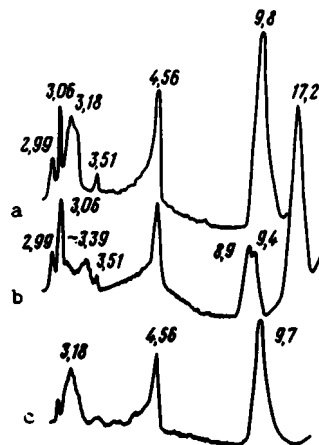


Fig. 6

Fig. 5. Diffractograms of sample 1583. A) Diffractograms of specimens prepared from tube aggregates; B) from dendritic "overgrowths"; a) air-dry; b) saturated by glycerine; c) fired at 550°C.

Fig. 6. Diffractograms of sample 16416, specimens a) air-dry; b) saturated by ethylene glycol; c) fired at 550°C.

structured "platelets," often with drawn out edges in the form of tails. Such book structure platelets comprise either a continuous network of particles (Fig. 2a) or characteristic lepispheres with sizes from 30 to 100 μm (Fig. 2b). The lepispheres are often concentrated in fibers. Locally, the lepispheres have an elongate form and a "crystallomorphic" space is observed inside them (Fig. 2c). They are abundant on some regions of well faceted "platelet" spaces, they are distributed side by side, and clay minerals form casings on them (Fig. 3a, b), but they also sometimes develop the form of lepispheres inside spaces, while they may almost completely "replace" them, so that the relicts of the initial crystal forms disappear.

Mineralogy. All of the cited samples were studied by the method of quantitative x-ray phase analysis. Diffraction patterns of samples 1541 and 1519 are practically identical with the diffractograms of monomineralic hydrated talcs. In the natural state, oriented specimens are characterized by diffractograms containing a series of basal reflections that is close to integral, with interplanar spacing d equal to 9.70; 4.79, and 3.17 $\text{\AA}$. The diffractograms practically did not vary after firing of the samples at 550°C (Fig. 4a, c). Saturation of the samples by ethylene glycol slightly displaces the first basal reflection to the side of large angles θ and leads to a marked weakening and widening of reflections from $d = 3.17 \text{ \AA}$ (Fig. 4b). The presence of the above described diffractional effects, as well as the magnitude $d(060) = 1.530 \text{ \AA}$ indicate that the structure of the studied samples at 90-95% are composed from talc, that is, high magnesian electroneutral 2:1 layers of composition $(\text{Mg}_{3-x}\text{Fe}_x)^{2+}\text{Si}_4\text{O}_{10}(\text{OH})_2$. In the microcrystals these layers statistically are disorderly transposed by saponitic or stevensitic layers, the concentrations of which do not exceed 10%. The distinctive feature of the hydrated talcs is that they are characterized by an exceptionally small thickness of regions of corregation distance (50-150 $\text{\AA}$), which is the basic cause of the disruption of integrality in the position of the basal reflections on diffractograms of samples found in the natural and dehydrated post-firing states.

Data of x-ray microprobe analysis, obtained for sample 1541 [in %: SiO_2) 62.25; Al_2O_3) 0.47; FeO 3.77; MgO 29.41; Na_2O 0.17; K_2O 0.16], is recomputed to an anionic form of $\text{O}_{10} \times (\text{OH})_2$ (at 1/2 content of elemental unit), gives a mineral formula: $\text{Na}_{0.02}\text{K}_{0.01}(\text{Fe}_{0.20}^{2+}\text{Mg}_{2.81}) \times 3.01(\text{Si}_{3.96}\text{Al}_{0.04})_4\text{O}_{10}(\text{OH})_2$, which completely corresponds to the above discussed presentation on the structure of the described mineral.

Dendritic-appearing "overgrowths" and tubular fibers were taken from sample 1583 and individually studied under a binocular magnifying glass. Figure 5 (column A) shows diffractograms of oriented specimens obtained from samples ground in water and settled onto glass tubes. The presence of two low angle reflections with $d = 13.7$ and $9.9 \text{ \AA}$, along with the $d = 3.19 \text{ \AA}$ reflection characteristic of hydrated talcs, indicates that the sample represents mechanical mixture of saponite and hydrated talc. The presence of a saponite phase is indicated by the fact that after saturation of the sample by glycerine, a

rather sharp and symmetric, although also low intensity, basal reflection 005 with $d = 3.59 \text{ \AA}$ is also recorded on the diffractogram, together with a sharp and intense reflection from $d = 18 \text{ \AA}$. Its absence on the diffractogram from the specimen found in its natural state uniquely confirms the presence of saponite in the sample.

The second phase of the "tube" part of sample 1583 is hydrated talc or a mixed layer phase of talc-saponite with a small number of expanding layers and a small thickness of coherent scattering regions. The high magnesian quality of the talc and saponite layers is indicated by the position of the reflection 060 with $d = 1.530 \text{ \AA}$, which is characteristic for these minerals, as well as by data of x-ray microprobe analysis, %: SiO_2) 56.28; K_2O) 0.34; Na_2O) 0.20; Al_2O_3) 2.49; MgO) 25.53; FeO) 6.00. For recomputation of the chemical composition to an anionic form $\text{O}_{10}(\text{OH})_2$ (at 1/2 content of elemental form) we obtained the formula $\text{Na}_{0.04}\text{K}_{0.02}(\text{Al}_{0.05}\text{Fe}_{0.34}^{2+}\text{Mg}_{2.62})_{3.01}(\text{Si}_{3.85}\text{Al}_{0.15})_{4.00}\text{O}_{10}(\text{OH})_2$ reflecting an averaged cationic composition 2:1 of layers of hydrated talc and saponite.

The main distinction of the phase composition of the strictly "dendritic" components of sample 1583 from the above described components is the higher content of hydrated talc in relation to saponite. It is also impossible to exclude the closer intergrowth of talc and saponitic structures, that is, the mixed layer formations of "saponite-talc" with a high degree of segregation of saponitic and talcic layers. We note that the diffraction pattern from an oriented preparation found in its natural state is also possible to interpret as result of alternation of $9.5 \text{ \AA}$ talc-similar and $14.4 \text{ \AA}$ saponite layers, although such a treatment of diffraction effects should only be considered as proposed (Fig. 5, column B).

Unusual diffraction characteristics were detected for sample 1614b (Fig. 6). The diffractogram, obtained from an oriented preparation deposited on a glass backing from a water suspension, is practically identical with the diffraction curve from hydrated talcs, since it contains intense basal reflections with d equal to 9.8 and $3.18 \text{ \AA}$, and a band of a two-dimensional diffraction of 02 with $d = 4.56 \text{ \AA}$. It is important to stress that the analyzed layer silicate, as in the hydrated talc, practically does not expand in the water medium. However, after saturation of the sample by ethylene glycol, the diffractogram recorded a strong basal reflection with d equal to 17.2 ; 9.4 , and $8.9 \text{ \AA}$. If the reflection from $d = 9.4 \text{ \AA}$ is taken as hydrated talc, then the first and third reflections indicate the presence of an interlayered phase in the structure, which contains approximately even proportions of a $9.5 \text{ \AA}$ non-expanding and $17 \text{ \AA}$ expanding layers. Provided that the latter do not expand with water, as this is a property of saponites and stevensites, but adsorb molecules of ethylene glycol, it is appropriate to call them expanding talc. Mixed layered phases of a similar type have not been described before, although the possible existence of unusual talclike minerals which expand not with water but with processing with ethylene glycol, has been shown in an example of synthetic compounds [2]. Apparently, the formation of phases intermediate in properties between talc and saponite is determined by the quantity of negative charge 2:1 of layers, caused by the substitution of Si for Al in the tetrahedra. In the absence of such replacement, as is characteristic for talc, the layers are electroneutral and do not expand either in a water medium or in organic liquids. For the degree of substitution of Si for Al in the 2:1 layers typical for saponites (more than 8%), molecules of H_2O and ethylene glycol are able to penetrate between the negatively charged 2:1 layers, leading to the appearance of expanding properties. For an intermediate degree of substitution of Si for Al in the tetrahedra, the "wedging" action of the H_2O molecule proves to be insufficient to separate adjacent 2:1 layers of the mineral, while the more polar molecules of ethylene glycol still are able to penetrate into the interlayer spaces of the microcrystals.

Discussion. Clay deposits of hydrothermal genesis are known from many regions in active spreading zones of the ocean. They are generally high temperature smectites, in particular nontronites, sometimes with a significant admixture of manganese hydroxides. They may be mixed with regular pelagic material and in their depositional form (lenses, layers, packets) they are similar to proper sedimentational accumulations. It is apparently possible in many cases to relate such "stratiformal nontronites" to hydrothermal-sedimentary formations, since hydrothermal material is spread and redeposited by currents. However, nontronites close to conditions of deposition may also be generated without redeposition by the diffusive carrying out of fluids [5]. Nontronites are often found directly on basalts. Their position is similar to frequently observed "overbasaltic sediments," in varying degree enriched by iron and manganese oxides.

In the Guayamas depression clay material is a component of most hydrothermal structures. It has unusual morphological structures and special mineral properties. Lepispheres, solid

dendrites, and sintered precipitates are characteristic. These are usual for the recrystallization of primary gel material (in the given case of magnesian silicates?!). The latter often overgrew crystals, with only spaces left, and possibly biogenic formations (judging by form they could have been bacterial colonies).

The main feature of the considered clay products is the magnesian composition (talc-saponite), and not the predominance of iron composition which is usual for hydrothermal clay formations in oceanic rift structures. In order to consider a possible answer to this question, we will consider the features of such an environment where the talc saponite association formed.

Although the hydrothermal fields in the Guayamas basin are also located within the limits of the spreading structure of the East Pacific rise, the physical-geographical conditions here are significantly distinct from other portions of this structure which are located in the open ocean. The basin represents a semi-isolated depression, where water exchange with the ocean is inhibited, and the floor has a zone depleted in oxygen. All sediments here are reduced (the carbon content is 2-4%). Leaking of liquid bitumen is locally observed close to the hydrotherm discharges, and sometimes there is saturation of the very hydrothermal formations. Thus, the medium into which fluids entered was substantially different than the middle ridges of the open ocean.

Another feature is the absence of basaltic extrusions on the floor of the basin. Basalts are found at a depth of nearly 500 m and are covered by sedimentary terrigenous-siliceous sequences of later Quaternary age. The sedimentary sequence contains, as was pointed out, dikes and sills of dolerites. Wells were drilled into the basin, and several (well 477, 481) are located on hydrothermal fields.

Processing of material from the wells made it possible to recognize the effects of near-surface intrusions (sills) on the surrounding deposits. Sediments next to a thick sill (well 477), particularly below it, disregarding the small depth of deposition, were lithified, their biogenic structure vanished, and a complex of newly formed minerals appeared: quartz, abundant anhydrite, sometimes with gypsum, dolomite (isotopic temperature of formation 100°C [4]) and calcite. The increase in the magnesium content in the sediments is a particular contrast. The composition of interstitial waters close to the sill is also altered [3]. We note an increase in the content of magnesium sulfates, as well as a decrease in silicon, while the value of Mg/Al increased and Si/Al decreased in the sediments. Thus, introduction of Mg occurred here, with it appearing in both solid and liquid phases. Carrying out of the silicon whose content in the sediments was initially very high also occurred here. It is assumed [6] that the sills served two purposes in the alteration of deposits; first, they impeded heat and fluids which were entering from below, creating a semiclosed hydrothermal circulation system; second, they separated heated interstitial fluids at the moment of intrusion and mobilized specific elements. Apparently, in this case, the "shield" effect of the sills has a primary value.

Finally, we note that in the hydrotherm "discharge" zones, the pH values of the solutions are lower than those peculiar to oceanic water.

Thus, silicate formation occurred for increased (not below 100°C) temperatures in a reduced environment in a neutral or weakly acid medium with high concentrations of Fe^{2+} , Mg, and SiO_2 . Recomputation factors were favorable to the formation of talclike silicates, in which the tetrahedral networks contain practically only Si cations. The extremely low degree of substitution of Si for Al was determined mainly by the amphoteric properties of Al, while the reduced environment prevented entry of Fe^{3+} cations into the tetrahedra. In these conditions, disregarding the predominance of Fe^{2+} cations, Mg cations proved to have the leading role in silicate formation. This is mainly connected with steric limits caused by the significant differences in ionic radii of Mg and Fe^{2+} . If lateral congruence of the Si-containing tetrahedral and Mg-containing octahedral networks for their combination in 2:1 layers is reached relatively easily, particularly for increased temperatures, then this agreement should break down with an increase of Fe^{2+} in the octahedra. The limited degree of substitution of Mg for Fe^{2+} in natural talcs is precisely connected with this circumstance. The content of Fe^{2+} in saponite octahedra increases somewhat as a result of the increase in the lateral sizes of the tetrahedral networks caused by the substitution of Si for Al.

The correlation of monomineralic hydrated talcs, which contain practically no Al in the tetrahedra, to places where hydrothermal sources are discharging is in agreement with the

above discussed concepts (sample 1541). The occurrence of saponites is recorded in more outlying regions, where, apparently the alkalinity of the medium relatively increased (sample 1583).

Comparison of the above presented structural formulas for sample 1541 and 1583 confirm the above cited considerations. In the case of monomineralic hydrated talc, the practical absence of isomorphic replacement in the tetrahedra is accompanied by very little content of Fe^{2+} in the octahedra. The appearance of a saponitic composition in sample 1583 leads to a significantly higher degree of replacement of Si for Al in the tetrahedra, and almost twice the content of Fe^{2+} in the octahedra.

The fact of the predominance of newly formed Mg-containing silicates in local portions of the main discharge of hydrotherms in the Atlantis II basin [1] is apparently also connected not so much with the high temperature, as with the features of the medium of mineral formation which impede the formation of silicate arrays, bands, and networks, in the tetrahedra of which, apart from Si, other trivalent cations may be contained. This in its turn significantly limited the possible participation of Fe^{2+} cations in silicate formation.

At the same time, based on the discussed position, it is easy to explain the formation of Fe-smectites in deposits developed on the limits of channels of hydrothermal discharge. Alteration of the oxidizing-reducing and acid-alkaline environments significantly expands the possibility of substitution of Si for Al and Fe^{3+} , which provides conditions for the formation of smectites, the octahedra of which are filled principally by Fe^{2+} cations. Subsequent processes of recrystallization or internal-structural oxidation of ions of Fe^{2+} lead to the formation of nontronites.

Thus, the formation of Mg-containing silicates is connected not with anomalously high enrichment of hydrotherms by magnesium, but with the limited degree of substitution of Mg for Fe^{2+} in the octahedra of 2:1 layers, which, disregarding the predominance in hydrotherms of Fe^{2+} , is determined by limitations to the entry of the trivalent cations Al and Fe^{3+} into the tetrahedral networks of these layers.

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EVOLUTION OF SEDIMENT ACCUMULATION PROCESSES ON SLOPES AND
THEIR RELATIONSHIP TO CLIMATE CHANGES

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The study of slope deposits led to identification of the evolution of sediment accumulation processes under unstable climatic conditions that existed between periods of climatic warming and glaciation. The discontinuous nature of colluvium formation, soil development and episodes of gravitational laminar-plastic downslope flow of rocks, associated with mudflows and landslides has been established. Lithologic and mineralogic characteristics of slope deposits are discussed.

The Quaternary has been characterized by climatic fluctuations. However, the evolution of sediment accumulation processes during transitions between glacial and interglacial times and between stades and interstades has not yet been sufficiently studied. Little attention was paid to sediment accumulation processes on slopes, although they are of prime importance in solving the paleogeographic aspects of general problems, relevant to the theory of lithogenesis. Sediment accumulation on slopes is among the first stages of initial sediment transport in the mobilization zone and is closely tied to climatic conditions. Interpretation of ancient slope deposits helps in the thorough definition of paleoclimatic conditions.

Characteristics of contemporary sediment deposition on slopes have been repeatedly investigated in various landscape-climate zones. Attempts have been made to establish the time sequence of slopes that formed during the Quaternary. A review of the pertinent literature led to two important conclusions. The first involves a climatically induced break in the slope deposition processes. In essence, during warming periods the slopes became covered by a soil blanket and slope processes tapered off. During periods of cooling, on the other hand, the vegetation thins and the slope processes intensify. Second, it was discovered that the periglacial solifluction deposits on slopes often are associated with cryogenic, freeze-related decomposition. This was an important accomplishment of the Quaternary researchers. The scientific foundation of this finding was first established by Moskvitin [8]. Later Tseitlin [12] identified patterns of temporal variation between various permafrost disintegration processes in the periglacial zone, related to stages of glaciation. This is how the questions emerged with regard to the evolution of periglacial zone permafrost processes [1, 12]. That evolution involved a change from a period, characterized by solifluction-type deformations, typical of the initial glaciation stage, to a period of maximum freeze-disintegration through permafrost, ending in the final glaciation stage. These were important conclusions. However, according to researchers who utilized the study of ancient permafrost processes in their approach, colluvial deposits disappeared almost completely at this stage. These sediments are widespread on slopes of the periglacial zone where they are among the most typical slope deposits. Indeed, as one considers the discussed evolution of the permafrost-related decomposition processes, it appears that simple colluvial processes do not exist under these conditions. The presence of permafrost generally is unfavorable for colluvium development.

The main thrust of the present paper is an examination of slope sedimentation processes during transitional stages between warmer and glacial periods. Samples taken at Kostenki, Voronezh District, have been investigated. For a number of reasons, the area is well suited for the study of this problem. First, a sufficiently thick blanket of complex slope deposits is exposed in deep ravines and gorges. Second, numerous Upper Paleolithic archeological

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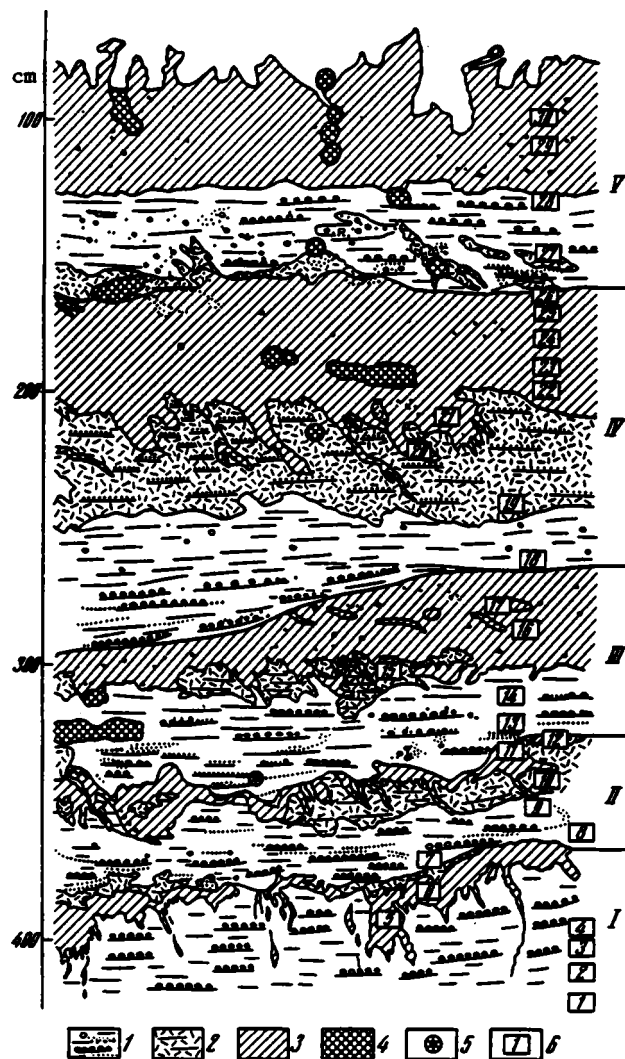


Fig. 1. Structure of slope deposits in pit #1, Kostenki-1 location: 1) colluvium; 2) portions with intensive secondary carbonatization; 3) buried soils; 4) krotovinas; 5) mammal bone fragments; 6) sample number; I-V) sediment cycles.

sites, studied for over a century, are associated with these deposits and provide age definitions. This is essential in estimating the intensity of slope deposition processes and their changes with time. In addition, the biostratigraphic material provides a very reliable tool for the reconstruction of conditions that prevailed on the slopes during sediment accumulation.

In the course of investigating archeological sites in the area, attention was repeatedly paid to slope deposits. Colluvial deposits include traces of soils, deformed by permafrost processes, as reflected by the presence of solifluction structures and incipient frost cracks. However, until now slope deposits have been discussed only in the most general terms, without lithologic and paleoclimate analysis.

Our most detailed information on the composition of slope deposits came from the study of exploration pits at the Kostenki-1 location. The following discussion is based mostly on the main results that were obtained in the study area, although data from other regions have also been used in discussing general problems.

GENERAL CHARACTERISTICS OF SLOPE DEPOSITS

Slope deposits at Kostenki-1, in addition to archeological excavations have been perpetrated by two exploration pits. The first pit, c. 4 m deep, revealed mostly colluvial layers,

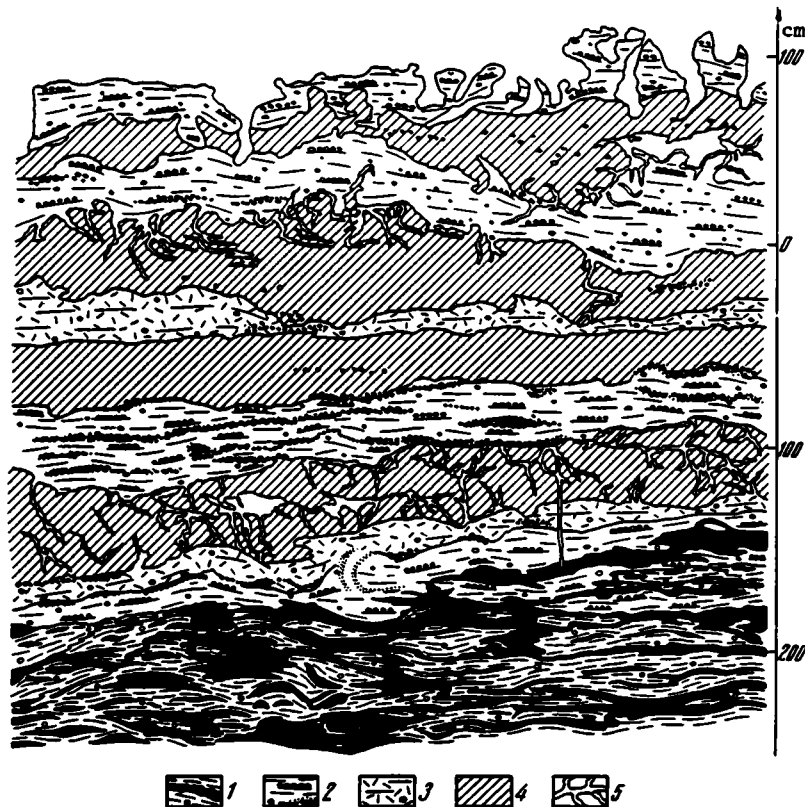


Fig. 2. Structure of slope deposits in the Kostenki-14 excavation: 1) fragments of humus-bearing buried soils; 2) colluvium; 3) portions of intensive secondary carbonatization; 4) buried soils; 5) fractures in soils.

represented mainly by pale yellow, brown loam, occasionally humus-bearing, with varying amounts of small gravel-sized and smaller limey marl particles in the section.* Buried soil horizons occur in the colluvium. The pit section displayed a number of soil-colluvium cycles (Fig. 1). Each cycle starts with a colluvial loam layer, occasionally with quite numerous marl-gravel fragments. The cycle is completed by a generally humus-bearing loam with very small amounts of pre-Quaternary rock fragments. The upper contact of the humus-rich layers is usually uneven and sharp. This indicates recurring periods of colluvium formation. Times of more and less intensive colluvium development alternated. As the result, at least five stages of colluvium formation have been identified, each capped by buried soil.

The analysis of the composition of colluvial deposits, in terms of the amount of the enclosed chalky marl fragments, indicates that during colluvium-forming Stages III, IV, and partly V slopewash was not intensive. Colluvial deposits at these times were primarily enriched in pre-Quaternary rock fragments.

At this time, the mechanism of colluvium formation should briefly be mentioned. The composition of the colluvium is significant. The unevenly distributed chips, clumps and poorly rounded pebbles of chalky marl form banded-lenticular concentrates, that "float" in the loam. Such a distribution of the detrital matter may only be explained by accumulation in mudflows that transport rock fragments. Under these conditions, most of the sediments exposed in the pit formed near the top of the colluvial body where such sedimentation processes are typical [6]. Deposits of the upper portion of the third stage and also the relatively uniform deposits on which buried soils IV and V had developed, resemble sheetwash deposits in terms of their forming processes. Two colluvial deposit types are thus known in this section. Their predominant formation conditions, or more exactly, the changes that influenced them over a time period, were associated with temporal changes of the physical geographic conditions during their accumulation.

*All experts in this area agreed on the colluvial nature of the slope deposits.

An additional, very interesting aspect of the section is the lower contact with humus-rich loams. A sharp, tongue-like contact is typical, probably the result of soil processes. In other words, the humus-rich layers are regarded as remnants of buried soils that subsequently have been mostly destroyed. Soil profiles have not been preserved in these layers. Of course, we cannot completely reconstruct the character of soil development from these fragments. However, as follows, information does exist to indicate the general temporal trend that involves these soil forming processes.

The study of the sections revealed the existence of a stage of intensive gravitational transfer of colluvial deposits, following their accumulation. A variety of gravitational processes were expressed in the geological record. The inclined position of the previously mentioned humus-rich colluvial tongues, in particular, was caused by the downslope movement of water-saturated soil cover.

Indications of gravitational transfer are also displayed by the analysis of the upper contact types of buried soils and their internal structures. As noted, the upper soil contacts in the studied section are generally abrupt and finely scalloped. Their interiors show no soil horizon development.

Inside the soils, especially in the oldest ones, colluvial humus-free loam inclusions of lenticular shapes do occur. The upper contacts of buried soils are characterized by a tongue-shaped variety, consisting of lingular wedge-outs of humus-rich loam, composed of buried soils. These tongues penetrate overlying colluvial layers. In the continuation of the tongues, the colluvium sometimes contains thin, humus-rich loam lenses. Such a contact may be interpreted as sedimentary structures entrapped by gravitation downslope movement over buried soils. This apparently explains the absence of certain horizons in the buried soils of these sections. Such horizons would have been destroyed during the downslope movement of soil and colluvial matter.

Available information supports our ideas about the character of the downslope sediment movement. The top units over the slope deposits displayed a primary heterogeneity. This is expressed primarily by rocks of various plasticity present in the colluvium and buried soils. This had predetermined the type of layering in the colluvial sediment blanket during subsequent gravitational mass movements. Thus, there exists a plastic downslope mass movement that rolls and flattens out the more plastic buried soils; destroying them in the process. In this case, we are dealing with a colluvial slope sediment cover, reworked by gravitational processes.

The intensity of gravitational mass movement on the slopes is defined by the plasticity of rocks, their water-saturation levels, the slope angle, and the depths of the various layers. The geological indicators of varying gravitational sediment transport intensities are especially well preserved in the exploration pit at the Kostenki-14 locality (Fig. 2). This illustration shows the following details: First, the flattened-out lower humus-rich buried soil layer is extremely well displayed. The roll-out process resulted in a parcel of mixed formations, composed of lenses of various forms of humus-rich loams and the light yellowish-brown colluvial loam itself. Furthermore, the structural details of the overlying buried soils are of great interest. The soil unit, second from the bottom, contains a network of mostly inclined fine fractures; a significant part of them penetrate the buried soil thoroughly. The fractures are usually filled by bleached, marly loam of high carbonate content. Parts of the inclined fractures display a smooth transition into subhorizontal fractures. Fractures are absent from the next buried soil horizon. The second buried soil horizon from the top fracturing occurs typically in the top portion and only on the left side of the sketched profile.

The fracture systems generally were caused by permafrost processes of desiccation. The fracture morphology usually was not considered in the publications. In our view, fracturing is related to gravitational downslope sediment movements and represents one of the first stages in the disintegration of continuous buried soil horizons. The differing degrees of fracturing reflect varying intensities in the gravitational sediment transport. In this context, the second soil from the bottom was torn apart by fracture development. It had disintegrated into blocks within its significant distribution area. In the second soil from the top, fracturing occurred only in the area, corresponding to the upper left-side of the sketch. Apparently, this represents the initial stage of fracturing and soil disintegration. The absence of fracturing on the right side of the sketch, in the same buried soil horizon, may be caused by fractures that segmented the soil matter into very small fragments.

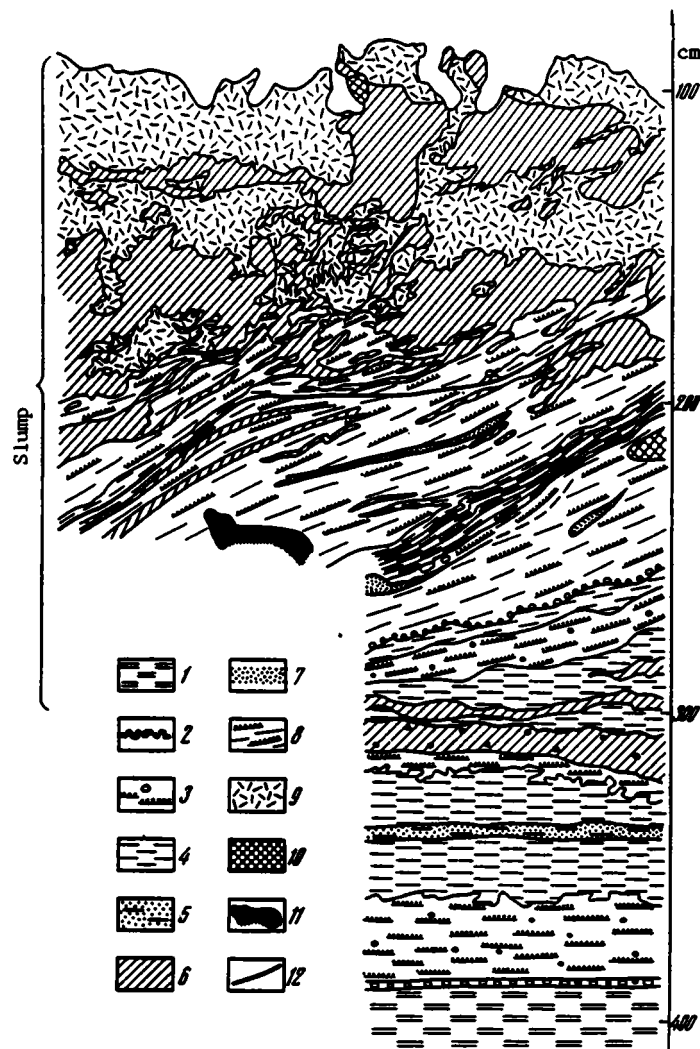


Fig. 3. Structure of slope deposits in pit #2 at Kostenki-1. 1) Weakly laminated brown loams; 2) gravel; 3) marllike pond deposits; 4) clayey sand; 5) sand; 6) buried soils, soil fragments; 7) volcanic ash; 8) admixed colluvium, pond deposits, buried soils, found in a slump block; 9) portions of intensive secondary carbonatization; 10) krotovinas; 11) large bone fragment; 12) zone of movement within slump block.

During such plastic gravitational flow events the top soil interval was completely removed. Finally, the total absence of fracturing in the soil unit, third from the bottom, may have been caused by erosion of the upper soil portion during plastic downslope transport of the layers.

Our data clearly indicate the uneven intensity of plastic downslope sediment flow, displayed primarily by the differing reactions of the transported units during these process. Furthermore, the gravitation mass movement of the slope deposits sometimes is complicated by slumps or large mudflows. The structure of beds, exposed by exploration pit Kostenki-1, serves as an example. This is located 25 m east of the original 1986 excavation. The section consists of two units: a lower, and an upper one that represents a slump block (Fig. 3). A slip surface zone is displayed at the base of the slump block, characterized by mixed matters of various origins. At least two internal thrust zones also occur in the slump interior. A complex, lenticular-banded interlayering of light yellowish-brown loam and marllike, light loam occurs here. The zones dip SW at an angle of 10-12°. The upper thrust zone displays fractured light-colored loam layer. Above this zone, at the buried soil horizon, rocks are

TABLE 1. Results of Spore and Pollen Analyses from Kosenki-1 Pit

Vegetation cycles	Spore-pollen complexes	Sample number	Lithology	Floral landscape	Climate characteristics	Number of cultural horizon	Climatic-stratigraphic division and subdivisions
XI	XVI	29-30	Brown loam with pseudo-mycelium - buried soil	Mixed-grass meadows with <u>Chenopodiaceae</u>	Subarctic, arid	I	Start of cool stade
X	XV	28	Brown loams with pseudo-mycelium, small amounts of chalk gravels and colluvium	Thinly developed (not dense) and isolated pine and spruce forests with mixed-grass meadows	Boreal-subarctic, relatively arid		Start of end of warm interstade
IX	XIV	25-27	Brown loams with pseudo-mycelium; chalk gravels and pebbles; at bottom: colluvium; top: buried soils	Thinly developed and isolated spruce forests, mixed-grass meadows	Subarctic-boreal and humid	Valdai	Start of warm stade
	XIII			Mixed-grass meadows	Subarctic, humid		End of cooling stade
VIII	XII	18-24	Brown loam, laminated, pale yellowish brown, numerous chalk gravels and pebbles, especially in the lower portion; at bottom: colluvium; top: buried soils	Taiga (spruce forests)	Boreal, humid	III	Warming of interstade
	XI			Thinly developed and isolated spruce forests, mixed-grass meadows	Subarctic, boreal, humid		End of cooling stade
VII	X	16-17	At top: low-humus loams; lower: brown loam with chalk gravel and buried soil	Gramineous mixed-grass meadows	Subarctic, humid		Transition to cooling stade
				Thinly developed, isolated spruce and pine forests	Subarctic-boreal, humid		End of stade warming
VI	VIII-IX	13-15	Top: off-white, marl-like loams; lower: pale yellowish-brown loam with numerous chalk gravels and pebbles. Iron-bearing microconcretions and colluvium	Forest steppe with pine and spruce, scattered linden trees, mixed grass meadows	Southern boreal, semi-arid	Middle	Maximum warming of interstade
V	VII	11-12	Humus-bearing loams, buried soils	Southern taiga (spruce forest)	Boreal, humid	VI	Warming, interstade

TABLE 1 (continued)

Vegetation cycles	Spore-pollen complexes	Sample number	Lithology	Floral landscape	Climate characteristics	Number of cultural horizon	Climatic-stratigraphic division and subdivisions
IV	VI	10	Off-white marllike loams, colluvium	Hydrophilic and mesophilic mixed-grass, gramineous meadows	Subarctic, humid	Early Valdai stage V	Cooling stade
III	IV-V	7-9	Pale yellowish-brown loams with numerous chalk gravels and pebbles, colluvium	Isolated pine- and birch forests. Also: gramineous mixed-grass meadows	Subarctic-boreal, humid Subarctic, humid		Start of interstade warming Cooling stade
II	III	5-6	Humus-rich loam with friable woody coal matter	Isolated pine, birch and spruce forests, with mesophilic mixed-grass meadows	Cool-temperate		Start or end of interstade warming
I	I-II	1-4	Top: brown loam; lower: pale yellowish-brown loam with marl pebbles and gravels. Also: iron pisolites and colluvium	Predominant grass and scrub associations represented by mesophilic meadows	Subarctic, semiarid		Cooling stade

intermingled to such an extent that one may assume presence of certain amounts of liquefied matter inside the slump block.

Our study of the sections and the carefully documented archeological sites indicate that the most intensive reworking during the plastic downslope transport of slope deposits involved the lower buried soils and allowed a better preservation of the upper buried soils. However, there is one exception to this general consideration of the reworked buried soils. This, in the long run, points to the complexity of the vector distribution as it applies to the gravitation transport velocity of the slope deposits. In this context, a relationship has been found in the first exploration pit with regard to the distribution of epigenetic carbonate from shallow ground water-fed springs. The distribution of epigenetic carbonate displayed a well-defined cyclicity in the section, expressed by its confinement to the upper colluvium section, found directly beneath the buried soils. This relationship disappears in Suite V of the colluvial deposits (Fig. 1). In this unit, epigenetic carbonate cementation occurs immediately on the buried soil, at the base of the colluvium. The epigenetic carbonate disappears upward in the section. This led to the assumption that a buried soil horizon had existed above this colluvial zone, destroyed during gravitational sediment transport. By now, not only the layering has been eliminated in the deposits, that were flattened and adjacent parcels displaced; individual units have been totally eliminated. In the end, this may hamper the detailed correlation of near-adjacent sections.

When did the gravitational mass movements of slope deposits take place and during what time intervals? As far as the question of time-span, it is known only that these were single-stage events. The time periods when the processes occurred can only be identified by the study of associated data, involving slope deposit ages and by the reconstruction of paleolandscape conditions, based on biostratigraphic information.

RECONSTRUCTION OF PALEOLANDSCAPE CONDITIONS DURING COLLUVIUM ACCUMULATION, BASED OF POLLEN AND SPORE ANALYSES

Study of sites of the Upper Paleozoic man in the Kostenkovsk-Borshchevsk Region revealed primarily the abundance of Upper Paleolithic mammal faunal remains, distributed between different cultural horizons. These results led to formulation of a general theory on the paleolandscape conditions for the time when ancient man inhabited this region. A cold tundra-steppe existed here in interfluvial areas and forests in the stream valleys [1-5].

Paleobotanists described the paleolandscapes in the most general terms (R. V. Fedorova, V. P. Grichuk, M. N. Grishchenko, and others). Only in the past few years have more detailed works been published [7]. The Kostenki-1 section that we did not directly study produced detailed palynological ideas with reconstructed landscape environments and paleoclimate characteristics, including suggested climatic-stratigraphic divisions and subdivisions (Table 1).

Certain important vegetational aspects that may be deduced from available data, should be noted here. First, the accumulation of colluvial deposits occurred in unforested and forest steppe (isolated patches of forests) environments. Under these climatic settings, the environments of colluvium accumulation prevailed within a wide range, from subarctic-humid to southern boreal semiarid conditions. Soils, exclusively on slopes and in ravines, formed mostly when forest conditions prevailed, weakening colluviation processes. The landscape settings and climatic conditions did not remain uniform. During Stage 2, for instance, the vegetation changed from gramineous mixed grass meadows to isolated birch-pine forests. At the end of this stage hydrophyllic and mesophyllic meadows predominated. The climate changed, correspondingly, from subarctic-humid to subarctic-boreal-humid; at the end, back again to subarctic-humid conditions. It is noteworthy that colluvium accumulation during the two lower stages occurred under conditions more humid than the drier stages that followed.

Based on palynological data, subarctic-semiarid conditions favored colluvium development the most. This were typical of the transition stage from a stade to interstade, and vice-versa. This also characterized the warmer, semiarid climatic optimum of the interstade, when arboreal forms played a small role. Open, treeless landscapes predominated during these stages.

The general conclusions, reached through pollen and spore work are in good agreement with the above-discussed general composition pattern of the section. An increase in slope transport during the upper stages of colluvium formation correlates well with the relatively arid conditions and the predominance of open (treeless) landscapes.

Palynological data and the composition of the section indicate a very important fact: quite sharp changes took place in the climatic conditions. The changes are reflected primarily by palynological data. These data and the radiocarbon dates indicate the dominantly Upper Valdai age of the studied deposits. The upper buried soil formed near the end of that stage. Thus, our data suggest that the Middle Valdai in the region was characterized by significant vegetation changes, corresponding to climatic fluctuations. The question arises whether the prevailing reconstruction of the periglacial paleolandscape should not be revised. Of course, our study area is far removed from the glacial margin zone that existed during the peak of the Ostashkovsk Glaciation. This may explain why, according to the pollen and spore studies such representatives of the hypoarctic flora as the dwarf birch Selaginella selaginoides are practically absent here. According to the literature, no indisputable traces of multiyear permafrost have been discovered either. The attempts by certain workers to relate minor deformation features to solifluction processes were geologically unfounded. In our view, soil deformations on slopes, due to solifluction, should be related to the laminar-plastic flow of water-saturated slope deposits. The thickness of sediments, transported in this fashion, is greater than expected for solifluction deposit. It reached 3-4 m at a number of locations. Therefore, the described gravitational laminar-plastic flow of matter should not be associated with general solifluction processes but rather related to so-called "tropical solifluction" processes. These are caused by thorough saturation of slope deposits. We believe that atmospheric precipitation was intensive in the subject area during the peak of the Ostashkov Glaciation. Thus, immediately following their accumulation on slopes, the saturated sediments, without significant interruptions, have undergone gravitational down-slope slumping.

This last process apparently is correlatable with spore and pollen data. The discontinuous pollen spectra provided a fragmental and incomplete record of the climatic rhythms (Table 1).

LITHOLOGIC COMPOSITION OF SLOPE DEPOSITS AND ITS CHANGES DURING TRANSPORT AND SUBAERIAL DIAGENESIS

Chalklike marls play a dominant role in the composition of slopes, immediately adjacent to the discussed deposits. Upper Cretaceous glauconitic sandstones with small phosphoritic concretions and older Quaternary deposits occur in adjacent areas. The preceding discussion on the lithologic composition of the slope deposits clearly shows that it was inherited from deposits that form the slopes. The abundance of detrital matter that consists of chalklike marl and the increased carbonate content of the layers also indicates this indirectly.

It is natural that all studied deposits include varying amounts of carbonate content. The colluvial loams and the upper soils had a carbonate content of 30-40%, parts of the section, enriched in secondary hydromorphic carbonate, contained 55% carbonate. Only the lower two buried soils had less carbonate content (7.24% in the lower soil and 25% in the second soil from the bottom).

During colluvial sediment accumulation, resulting from the reworking of the predominantly chalky rocks, these rocks disintegrated gradually, primarily displaying a declining trend in the original carbonate content.

Volcanic ash, concentrated in thin lenses and laminae was the only exotic matter in the colluvium. It was characterized by pale yellow color and silt grain size. Under microscope, the colorless glass fragments appeared as angular, isometric, elongated and bifurcating particles. These appear to be fragments of very thin partitions between gas vesicles that formed during expansion and disintegration of individual portions of an original gas-rich melt.

The main colluvial deposits in all of the identified cycles have similar composition. They are light brown or pale yellow loams with uneven concentrations of gravel, angular fragments and slightly rounded pebbles, composed of chalky marl. Occasionally, the detrital matter was displayed in the pit walls as concentrations of discontinuous "chains" or thin lenses. In each colluvium deposition stage the detrital matter concentration, as a rule, decreases upward in the section. This indicates a gradual decline in the intensity of the sediment accumulation process.

Thin section study of the rock groundmass showed that it is composed of carbonate fragments among which a limited number of individual carbonate grains, molluscan shell fragments,

fragmental and complete foraminifer tests and echinoid spines, fragments of pelitic organic limey rocks and finally, rounded or elliptical-shaped carbonate muds or silty-carbonate aggregates. These range between 0.2-0.7 mm and consist mostly of pelitic carbonate mass with quartz grain inclusions, shell matter, etc. The aggregates are mostly loosely compacted. As the result, pores are common in the rock, although occasionally filled by silty-pelitic cement mass that resembles aggregate matter.

The rounded aggregates form the very typical, so-called roll-like ("katun") internal rock structure that in our case is characteristic of colluvial sedimentation.

The silicate rock component ranges between 2-5%. Angular-rounded quartz grains predominate. Individual K-feldspar, glauconite, muscovite, phosphate grains, as well as silty-clayey, carbonate-free microconcretions, colored by iron hydroxide, also occur. The presence of silicate matter suggests that colluvium accumulation occurred not only due to slope wash-transportation of the carbonate matter and its subsequent destruction, but also through the mixing of various sediment types, located on the slope.

In general, the rock is perforated by rare rounded pore canals. There are small ones, with a diameter of maximum 0.25 mm, and rounded ones with a diameter of maximum 1.0 mm. The small ones resemble phytopores. The larger ones, probably were partly burrows of mud-eating insects. This is indicated in particular by fine nodular earthen "plugs," typical in some of the pores. The thin pore walls in the lower part of the section usually are covered by a whitish carbonate film, while in the upper portion, by golden-yellow algal encrustations. In deposits of the last colluvium-forming stage, some pore walls are covered by lubinite (moon-milk).

Another important characteristic of the discussed colluvial sediment is the presence of bright, marl-like portions of clayey-limey loams that occur almost exclusively in the upper interval. The only exception are deposits of colluvium-forming Stage V. In contrast with all the rest of the deposits, the base of that interval consists of lenticular patches of clayey-limey loam.

The clayey-limey marl-like loam also contains detrital marl. In contrast with the previously described colluvial deposits, the investigated parts of the loam display intensive carbonate enrichment, accompanied by the dissolution and partial metasomatic replacement of silicate and carbonate fragments. Pelitic carbonate cement fills pores in the loosely packed matter between the "rolls."

In general, we believe that the intensive secondary carbonatization was caused by ground water discharge.

Vertical columns of marl-like loam, found in the first exploration pit are believed to be relicts of ground water feeder canals. These provide direct geological evidence for the past existence of artesian springs.

Finally, the colluvium locally contains small organic-iron pisolite concretions in the first, third and fourth colluvial horizons.

Let us now review of humus-rich layers. The section displayed evidence for soil formation. Pollen and spore studies indicate that these soil-forming stages coincided with periods of forests and treeless vegetation in the area, characterized by humid-subarctic climates during which mixed-grass gramineous meadows predominated. For this reason, the stages, associated with traces of soil formation presently are briefly characterized by these two vegetation types.

Soil horizons I, II, and IV represent forest soils. These are distinguished by their color and the preserved internal structure that earlier has been attributed to colluvial deposits. Fulvate-type humified plant remnants occur in the first soil horizon. The clayey groundmass is macropelitic, tangled-fibrous. Well-oriented clay crystals appear against this background, mostly along certain pores that occur in poorly packed matter and in lithogenetic fractures. In most instances, organic-iron compounds stained the clayey sinter aggregates to various degrees. They often form small, rounded, almost opaque aggregates of diffuse contours and 0.2-mm diameter. Small iron pisolites also occur.

The soil horizons also contain nests, thin whitish yellow veins of epigenetic, pelitic carbonate matter. It is most significant that in contrast with all higher soil horizons, the lower soil horizon contains no inclusions of large or smaller marl fragments. These apparently had been totally dissolved.

Horizons III and V formed during treeless stages. They are slightly humus-stained, slightly compacted, carbonate-bearing, with marl fragments and carbonate-free "rolls" and rare impregnations, strongly stained by reddish-brown organic-iron pigment. Soil horizon V contains significant amounts of biogenic canals, with limey encrustations of limey golden-yellow algae. The large pores and parting surfaces carry abundant lublinitic precipitates. The studied deposits displayed both sedimentary and epigenetic characteristics.

The sedimentary characteristics are primarily shown in the textural and structural properties. Thus, the gravelly-pebbly and sandy-silty sediment components changed quantitatively from layer-to-layer, while qualitatively remained uniform throughout the entire investigated interval. This indicates a stable source area of the sedimentary matter. Furthermore, the roll-structures with characteristic pores that occur in the loosely compacted matter, in all the studied samples to various degrees may be explained by epigenetic carbonatization. Colluvial setting dominated sediment deposition.

The next group of sedimentary features reflect paleoclimatic conditions during formation of the sediment train. They include variations in the relative composition of sandy-silty carbonate fragments, derived from chalky source matter. Buried soils are also considered here.

The presence of subaerial detrital carbonate sediments, easily affected by atmospheric precipitation, reflects various aspects of semiarid climatic conditions that existed here.

Variations in the composition values of sandy-silty carbonate components, derived from chalky sources (chalky rock fragments, foram tests, echinoid spines), as well as the degree of corrosion of these fragments may be interpreted as indicators of changes in the amount of precipitation. It may be concluded then that the carbonate particles in the section reflect at least three phases of increased precipitation. The first occurred during the development of buried soil horizon III. Detrital particles in this horizon were high in carbonate content, due to the presence of skeletal fragments of chalky marine organisms. They all displayed indications of corrosion and their concentrations were smaller than in the lower and upper layers. The second phase with relatively higher precipitation rates corresponds to the formation stage of buried soil horizon V. Its effect on carbonate sediment accumulation differed little from the previous one.

Carbonate sediment accumulation was interrupted, practically totally, only once in the geological evolution of the sediment train in question; during formation of buried soil zone I. The sediments contain almost no sandy-silty carbonate components but possess rare, coarse sand-granule-sized carbonate fragments. This is explainable by the fact that sediments of this layer formed during a climate of substantial humidity. Dark-colored, silty-clayey, carbonate-free rolls occur in this soil as rock-forming components of the loamy groundmass. Optical data indicates that the humified plant fragments are of the fulvate variety. Optically oriented clay incrustations occur in the loam groundmass. They are colored by organic-iron pigment. Small organic-iron concretions also occur. This supports our idea about the existence of forest soils and corresponding forested landscapes.

The humus coloration in buried soils II and III optically corresponds more to humate than to fulvate. Based also on other data, this indicates that at this time soil formed under isolated forests, in a setting that resembled a forest-steppe landscape.

The syngenetic features also include hydrogenic carbonization, expressed in certain portion of the section by a sharp increase in the concentration of cemented pelitic carbonate matter. It filled sedimentation pores and metasomatically replaced silicate and carbonate fragments in sandy-silty loam components by various processes. Parts of the section that were influenced by intensive secondary carbonatization are distinguished by their white coloration. These also occur in the discussed fine breakage fractures.

Development of a portion of the sediment sequence with higher carbonate content is related to ground water springs, highly enriched in bicarbonate. The springs resulted from increased atmospheric precipitation during the peak of the last glaciation. Water-saturation of the deposits led to gravitational, plastic downslope mass movements processes. The presence of a zone with hydromorphic carbonatization in the upper part of the colluvial beds may have resulted from the presence of soil horizons and colluvial zones of various permeabilities; also from solutions, expelled from the zone of more intensive plastic flows. The increased clay content in soils of the discussed area of slope deposits apparently led to more intensive plastic flow-type mass wasting processes.

The epigenetic characteristics include biopores, colonies of golden-yellow algae and lublinitite precipitates.

Biopores, the overwhelming majority of which were phytopores, penetrated the entire bed, down to 4 m beneath the surface. For this reason, their density increased upward in the section. The epigenetic nature of the biopores is indicated by the fact that they perforated layers that have undergone various degrees of alteration through hydrogenetic carbonization. Apart from earthen plugs, found in burrows of mud-eating organisms and incompletely disintegrated capillary root remnants in phytopores, these biopores remained empty. Only rarely, in the lower section intervals were pore walls coated by a thin pelitic carbonate film. In the upper section, colonies of golden-yellow algae and/or lublinitite precipitates occurred occasionally.

Thin section studies showed that the upper beds of Stages III, IV, and V (Kostenki-1) regularly contained isolated, calcified golden-yellow algal cells. Sediments of Stage III contained few of them, while in the lower portion of Stage IV they occur in lifelike condition. In sediments of Stage V the cells became the dominant components.

As indicated, golden-yellow algae are ephemerals under semiarid climatic conditions. Their distribution is associated with times of greater precipitation and episodic reoccurrences of ponds, steppe basins, and similar wetlands. During wetter periods, conditions turned unfavorable for the algae. Therefore, the appearance of golden-yellow algae in the upper portion of the section seems to have been associated with more arid conditions; such that existed after the intensity of gravitational mass movements diminished in the area.

The first minor lublinitite precipitates, needlelike calcite modifications, first occur in the middle portion of Stage IV, at c. 2 m depth. Its concentration increases upward and the increase continues up to the highest horizons of the section in question. In contrast with the golden-yellow algal colonies that encrusted only phytopores, lublinitite also occurs in any other void type: in pores of loosely compacted matter, parting fractures, and others. In this context, lublinitite may be considered an epigenetic product.

CLAY FRACTION STUDY RESULTS

Samples from the slope deposits have been studied by x-ray phase analysis, by diffractometer DRON-2 (CuK α radiation; Ni-filter). The diffraction patterns were from oriented, glycerine-impregnated samples, air-dry < 0.001-mm fraction, at 550°C temperature, and also after treatment with 10% HCl. The sample pairs were taken from the colluvium beneath the modern soil and from buried soils (samples 10, 12; 19, 22; and 28, 29). These were studied by the electron diffraction method of oblique (EDO) structures.

The clay fractions of all colluvium samples turned out to be monotypic, consisting of several components. Finely dispersed dioctahedral smectites predominate among the layer silicates. They contain structural defects. Disordered mixed-layer smectite-mica minerals were also present. A small but constant amount of illites, chlorite and kaolinite also occurred. Quartz and traces of feldspars represented tectosilicates. The Ca-calcite concentrations differed between different samples, and its content usually diminished in the buried soils.

X-ray results on the composition of the < 0.001-mm fraction are given in Figure 4.

Illite was analyzed on the basis of the 001 reflections in the diffraction patterns. The interplanar spacing of the first low-angle reflection was defined as 10.1-10, 9.9-9.8, and 9.9 Å, correspondingly, in an air-dried, glycerine-impregnated and calcinated state at 550°C. The shift of this reflection, with a range of $d = 9.9-9.8$ Å in glycerine-impregnated samples, indicates the presence of minerals that include ~10-20% expandable layers in the structure.

Chlorite can be confidently identified in the samples with several components by its 002, 003 reflections; d equals 7.1 Å, correspondingly, 4.72-4.60 Å. Glycerine-saturation of samples left the values unchanged. After heating at 550°C temperature, a reflection of $d = 13.5-13.8$ Å appeared. In comparison with 14 Å, the value was somewhat lower, indicative of structural defects (discontinuities) in the brucite layer of the chlorite structures.

The presence of kaolinites was established by treating the samples with 10% HCl-solution. The 001 and 002-reflections produced $d = 7.1$ and 3.56 Å values, correspondingly.

Because smectitic and smectite-mica mixed-layer minerals were the components most sensitive to changing conditions in the media, much of our interest was focused on them. We have

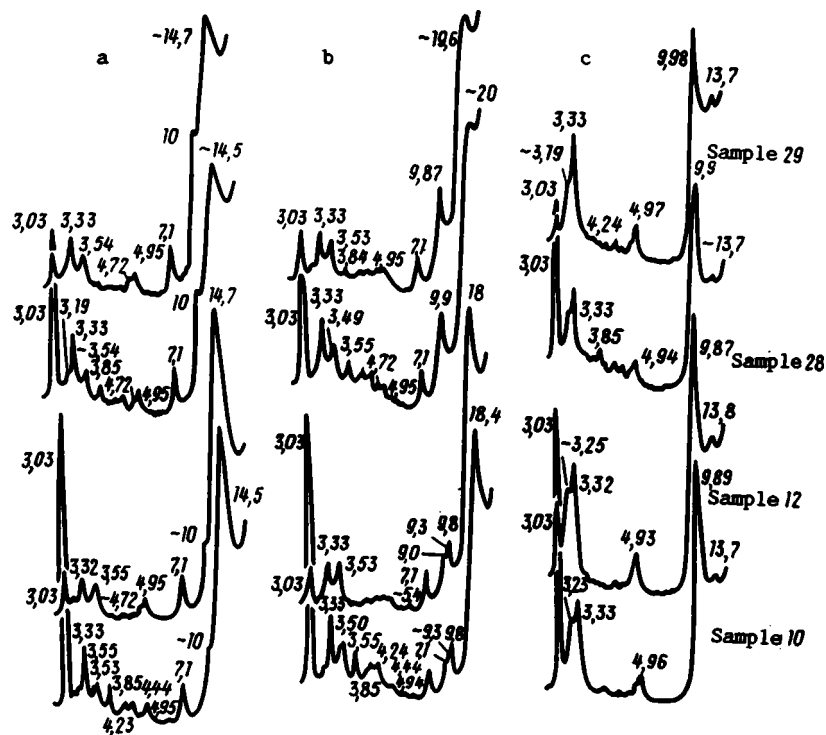


Fig. 4. Typical diffraction patterns. Samples 10 and 28) colluvial deposits; samples 12, 29) buried soils: a) air-dried sample; b) glycerine-impregnated sample; c) calcinated at 550°C.

observed and contrasted similarities and differences in the diffraction pattern characteristics of these minerals from various intervals of the section.

Finely dispersed dioctahedral smectites were common throughout the studied samples. These were identified in the diffraction patterns by the 001-reflection. The d-values fluctuated due to compositional differences. In air-dried condition the d-values of the first reflection ranged between 14.5-15 Å. This seems to have been caused by the predominance of Ca-cations in interplanar positions and by diminished Na and K cation concentrations. Glycerine-saturation of the samples led to a shift in the low-angle reflection with a value range of $d \approx 18$ -18.6 Å and the appearance of a reflection, with $d = 9.0$ Å (in smectites from the lower half of the section; smectite diffraction characteristics in the upper part of colluvial slope deposits will be discussed in the following). Strong 001 and 003-reflections appeared in all of the diffraction patterns after heating at 550°C. Their d-values were 9.9 Å, and ~ 3.19 -3.25 Å, correspondingly.

Along with smectites proper, samples from the lower section interval contained disordered mixed-layer smectite-mica. In a glycerine-saturated state, the samples displayed diffraction values of $d = 9.1$ -9.4 Å, indicative of mica-type interlayers in the crystal structures. This interlayer content ranged between 20-50% (samples 2-19, Fig. 1; samples 10 and 12, Fig. 4).

Dioctahedral smectite samples from the upper half of the section in glycerine-saturated state display low-angle reflections with $d = 18.6$ -20 Å. The higher this value, the poorer and more diffuse the reflection outlines are and higher the background dispersion level. Higher-order basal reflections are absent. It may be thus assumed that the mineral in question is a smectite and not a mineral with smectite-mica mixed-layer structure. This mineral is distinguished by its very high values of dispersion and structural defects. It was represented by samples 21-30, Fig. 1 (also, Fig. 4, samples 28 and 29).

Thus, along with the uniformity of the general phase composition of clay minerals, typical of all the studied sections, sediments of the upper section produced a characteristic smectite-type diffraction pattern.

In order to obtain more detailed information on the structural characteristics of smectitic and mixed-layer smectite-mica minerals, six samples have been selected for electron diffraction studies. These came from colluvial deposits beneath the modern soil and from buried soils (samples 10, 12, 19, 22, 28, and 29). In all samples the electron diffraction patterns of oblique structures (EDO) were distinguished by a raised background level of diffuse dispersion, indicative of the presence of significant amounts of amorphous matter. Reflections of a micaceous mineral, polytypic modification of $2M_1$ occurred in three samples (10, 19, 22).

Only reflections hko appeared in the EDO-reflections of the usual sample preparates, hkℓ-reflections were absent. Such patterns are typical of smectite minerals with disordered structures. Only b-values (9.00-9.02 Å) were identifiable for the disordered smectites, indicating a dioctahedral smectite structure.

1 n K_2CO_3 -solution was used in treating samples for the study of the structural ordering of the minerals. Subsequently, the samples were subjected to 70 cycles of wetting-and-drying. During this treatment, K remained the sole interplanar cation, located in the centers of hexagonal lattice cell configurations of 2:1 mixed-layer minerals. X-ray studies of K-smectites indicate that these minerals practically ceased to expand under both natural and ethylene glycol-saturated conditions ($d_{001} \approx 10$ Å). The K-smectites have also studied by the electron-diffraction method. Only hko-reflections occurred in EDO, as well as in natural EDO sample preparates; the hkℓ-reflections were combined into a uniform, diffuse background.

Under a micaceous process the superimposition of the 2:1 layers in the K-saturated samples the dislocation defects were eliminated. Therefore, the absence of the hkℓ-reflections, both with $K = 3n$, as well as with $K/3n$ values, indicates high concentrations of lattice defects in the K-smectite structures, caused by disordered azimuthal rotations of the successive 2:1 layers, by turn angles that were multiples of $n \cdot 60^\circ$ ($n = \pm 1, 2, 3$).

Thus, structural defects both in the natural and in the K-smectites did not reveal the characteristics of cationic distribution patterns in their 2:1 layers.

Comparison of slope deposit clay fractions with the phase composition, found in nearby bedrocks and discussed in detail by Murav'ev [9], established that the compositional characteristics were inherited.

Murav'ev proved that clay minerals in the insoluble residues of Mesozoic organogenic carbonate rocks are totally dominated by smectites and mixed-layer smectite-mica minerals. Very minor amounts of illites, kaolinite and tectosilicates (detrital quartz and feldspars) also occur. The carbonate matter is represented exclusively by $CaCO_3$.

Our studies have shown no significant differences in the mineral composition of colluvial deposits of the buried soils. This may be caused by two circumstances. First, the high carbonate content in rocks of the entire section resulted from an alkaline medium that favors 2:1 layer silicates. Second, the buried soils in the section either represent the lowest horizons, with almost unaltered, preserved primary minerals, or — under certain conditions — they represent incipient soil-forming processes. Such soil process indicators include an increase in the x-ray-amorphous matter of buried soils and a decrease in their Ca-carbonate content.

As noted previously, sediments of the upper half of the section are distinguished by the fact that their basic clay fraction component is a smectitic mineral with a diffraction pattern that indicates ultrafine dispersal features and the presence of structural defects. This part of the section contains the thickest archeological cultural horizons (horizons I and III). The abundance of organic matter and products of human life processes, related at these sites to ancient man, may have created active reagents. These influenced the chemical media that surrounded the studied clay minerals. The unusually high rate of structural defects found in smectites and absence of the mixed-layer smectite-mica phase, accordingly may be considered as the result of acidification by soil solutions that converted the mineral matter into amorphous substances. If this working hypothesis on the genetic connection between smectitic minerals and the thickest archeological cultural layers is confirmed by future studies, then the biological activities of ancient man actually did alter the mineral composition of the deposits.

* * * * *

The study of slope deposits revealed the short time interval of the evolution of slope sediment accumulation processes. This was the transitional period between the warming and the last glacial maximum, closely related to climatic changes.

Based on results of the spore and pollen analysis of the vegetative cover the climate was quite cold. On the other hand, there had been individual temperate-cold and even temperate climatic periods in the subject area. At the same time, there had been also periodic changes in humidity. Thus, the climate of the transitional period between climate warming and glaciation was distinguished by its instability.

The climatic changes, above all, involved repeated, abrupt intensity changes in the colluviation processes, very strongly expressed in the various buried soils. The most intensive colluviation occurred under subarctic-humid, semiarid conditions that were typical of landscape changes from stade to interstade conditions and vice-versa, as well as of the semiarid climatic optimum during the interstade. These plant communities produced open, unforested landscapes.

Precipitation increased sharply during the glacial maximum. This involved major trend shifts in sediment accumulation processes on slopes. The significant humidity increase during the glacial maximum resulted in saturation of the slope deposits, leading to gravitational plastic mass movements downslope, sometimes associated with mudflows and slumping. As the results, in certain areas the slope deposits partially or completely lost their primary characteristics. This, in particular, happened in buried soils and, to varying degrees, also in colluvial sediments.

The altered deposits reflect the first stages of the sediment mobilization process. Essentially, this process involves bedrock disintegration, displacement of various sediments, and, finally, results in the formation of new sediment types. These new sediments preserved the various traits of colluvial sedimentation, soil formation, and gravitational earthflows. Also preserved are sediment alteration features that resulted from changes in paleohydrogeological conditions, possibly even the impact of activities of ancient man, and processes that might have been associated with subaerial diagenesis.

The mineral spectra of the sediments were clearly inherited from bedrock. This was reflected in the carbonate content of the newly formed sediments and also in mineral mixtures from sediments of various ages that occurred in adjacent slopes. The carbonate content of the described sediments naturally was much lower than that of the chalklike marls. Therefore, probably there was a significant carbonate loss during slope sediment formation. The general trend of this loss, however, appears to be more complex. The extent of carbonate loss from the various buried soils was varied. On the other hand, during slope sediment accumulation the colluvium was enriched in newly formed carbonate matter. New mineral formations also include golden-yellow algae and lublinites. The presence of finely dispersed smectite with structural defects, among clay minerals in the upper part of the section, is a most important finding. Finally, the porosity of deposits was associated with subsequent reworking processes. After gravitational transport ceased, this reworking formed the slope deposits. This is why the pores remained open.

In contrast with other workers, we found no indisputable evidence for multiyear permafrost in this area. Many workers believed in the presence of various solifluction structures in the southern margin of the periglacial zone. However, no substantial evidence is yet available to support a genetic theory of these sediments that involves multiyear permafrost. Based on research and a review of the literature, we believe that gravitational mass movements of saturated slope deposits were widespread at the time of the glacial maximum. However, this downslope sediment movement was unrelated to multiyear permafrost. The rocks that participated in these mass movements, were involved in such plastic sediment deformation processes that were more comparable to tropical solifluction, even if the subject area did not resemble tropical regions in any way. The downslope sediment transport indicates a quite humid climate in the southern half of the periglacial zone during the last glaciation. We do not categorically deny the likelihood of permafrost in that area during the last glaciation. According to the literature, geological proof does exist for the presence of permafrost at a number of locations (e.g., in the western Ukraine), but only after the glacial maximum.

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RATIO OF ORGANIC AND INORGANIC COMPONENTS IN CERTAIN TYPES OF BLACK SHALES

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UDC 553.068.6

In the article, we discuss questions concerned with the quantitative interrelationships between primary components of carbon-bearing sedimentary rocks. We show that the content of organic carbon is determined by the composition of the rock.

In connection with the discovery of oil pools in the Bazhenov suite of Western Siberia, there has recently been significant interest in the Domanik-type deposits, a specific stratum of interlayered carbonate-clayey-siliceous rocks enriched in organic carbon, C_{org} . The Domanik formation is widely occurring on the eastern portion of the Russian platform, where it has been classified as an oil-source suite on the basis of geochemical data from many investigators [2, 5]. Despite the large number of studies, the place of highly carbonaceous varieties among the sedimentary rocks has not been adequately defined. There has been no unity in their classification thus far. A number of investigators have absolutized the inorganic components (carbonate content, clay content, silica content); others have absolutized the organic components (C_{org} , bitumen content) [4]. Researchers have not clarified details of the distributions and interrelationships of the four primary rock-forming materials in these deposits (carbonates, clays, silica, and organic material), which in combination represent a single system controlling the processes of oil formation.

The goal of our present researches consists in ascertaining the quantitative interrelationships between the primary components of carbon-bearing rocks. Rocks of a predominantly Domanik type in the Permsk Prikam'ye, the Southern Urals, the Western Bashkir, and Komi ASSR

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TABLE 1. Mineral Composition of the Rocks, %

No of points (see Fig. 2)	Occurrence area	Rock	No. of borehole and sample	Undissolved residue	SiO ₂	Clay	Σ carbonates	SiO ₂ (free)	Corg
1	2	3	4	5	6	7	8	9	10
Permskoe Prikam'ye*									
1	Borovitskii	Marl	605	34,70	23,90	19,14	55,35	11,68	0,52
2	Tunegovskaya	Limestone	37	18,91	10,46	10,64	74,22	3,67	2,36
3	Andreevskaya	Same	50	14,20	5,24	5,57	73,69	1,70	0,83
4	"	"	50	10,10	5,83	7,22	84,17	1,22	0,92
5	Lyzovskaya	Clay	107	70,17	42,51	66,59	3,62	0,00	6,03
6	Krasnosel'skaya	Limestone	197	15,56	12,56	9,76	75,81	4,84	1,84
7	"	Limestone, clayey	197	29,58	17,99	22,06	67,12	3,92	2,26
8	"	Limestone, slightly siliceous	197	15,88	9,75	10,75	80,11	2,89	0,52
9	Kirillovskaya	Same	101	17,22	11,61	10,31	76,53	5,03	4,09
10	"	Limestone, siliceous	101	27,60	22,98	8,47	67,94	17,58	1,37
11	"	Limestone	101	4,53	3,44	0,69	89,40	3,00	13,96
12	Turkinskaya	Limestone, siliceous	53	36,65	34,69	2,27	57,61	33,24	2,57
13	"	Limestone	53	4,42	3,18	2,05	94,84	1,87	0,89
14	"	Limestone, siliceous	53	45,54	38,41	10,93	39,51	31,43	11,67
Southern Urals†									
1	Basa River, Sample III	Silicite clayey	1(c)	82,36	74,41	20,81	3,06	61,21	4,90
2	Kush-Elga R. Hole 3	Siliceous-argillite	1/98	70,79	62,63	26,38	2,84	45,69	13,35
3	Same	Silicite clayey	2/97	77,93	73,01	15,82	2,33	62,94	11,37
4	Kush-Elga R. Hole 4	Same	3/93	84,90	80,06	15,90	1,97	69,94	5,62
5	Kush-Elga R. Basa R.	Silicite	4/94	85,60	81,16	16,57	1,65	70,57	5,24
6	"	Same	130(T)	-	74,41	20,81	3,67	61,21	4,90
7	"	Limestone	2(C)	31,24	27,48	7,59	60,97	22,69	2,35
	Sample I	siliceous							
8	"	Same	3(C)	60,43	53,21	16,63	25,42	42,63	3,40
	Sample II								
9	"	"	4(C)	54,31	49,14	12,46	37,11	41,35	1,50
	Sample IV								
10	"	Limestone	5(C)	23,79	21,88	4,13	68,72	19,25	1,60
	Sample V	siliceous-dolomitized							
11	"	Silicical-careous	6(C)	44,34	39,91	9,64	45,37	33,86	2,75
	Sample VI								
12	"	Silicite, calcareous	7(C)	59,38	56,38	7,52	30,78	51,58	3,00
	Sample VII								
13	Tokaty R.	Limestone siliceous	9/61	33,20	30,86	6,54	62,27	26,72	1,39
14	Shilkai River	Limestone clayey-siliceous	10/92	-	35,45	13,94	54,94	26,55	1,80
15	Ryauzyan R.	Silicical-careous rock	13/128	46,26	40,41	18,98	43,81	28,30	3,62
16	Basa R.	Limestone siliceous	128(T)	-	27,59	8,30	61,68	22,31	2,35
17	"	Silicical-careous rock	129(T)	-	53,42	18,72	26,19	41,42	3,40
18	"	Silicical-careous rock dolomitized	131(T)	-	49,30	13,95	36,39	40,40	1,50
19	"	Limestone siliceous dolomitized	132(T)	-	21,89	4,27	66,54	19,21	1,60

TABLE 1 (continued)

1	2	3	4	5	6	7	8	9	10
20	"	Silicical-careous rock	133(T)	-	40,04	11,0	46,02	33,0	2,75
21	"	Silicite clayey-calcareous	134(T)	-	56,51	10,24	31,39	50,00	3,00
22	Terekly R.	Silicical-careous rock	11/78	59,62	52,86	24,32	31,26	37,41	2,23
Western Bashkir †									
1.	Kul'tyuba	Silicite clayey	16/6	92,55	82,20	30,15	0,00	56,90	0,34
2	Cherkassy Well I	Clay siliceous	1/67	76,01	66,20	58,36	6,76	13,18	8,17
3	"	Marl siliceous	1/72	63,03	72,10	36,04	20,20	22,42	8,57
4	Cherkassy	Same	1/75	65,77	66,90	44,56	20,63	15,05	5,42
5	Sterlibatashevo	"	13,636	53,60	61,80	37,81	14,93	9,03	19,46
6	Chekmagush	"	65/1079	43,30	69,90	26,38	16,59	13,31	30,27
7	"	Siliceous-argillite	65/1085	65,72	73,50	35,09	16,72	25,96	9,80
8	Northern Kul'tyuba	Same	23/211	42,12	74,09	15,14	25,15	21,59	23,15
9	Yugomashevo	Silicical-careous rock	3/389	55,15	82,14	21,75	22,45	31,41	13,47
10	Or'ebash	Same	11/567	33,34	63,00	23,60	51,00	5,99	11,38
11	Kebyachevo	Limestone siliceous	3/51 747	23,40	75,60	11,19	48,92	10,61	10,06
12	Baikibashevo	Silicite calcareous	3/500	87,77	97,47	3,48	26,74	83,38	4,47
13	Yugomashevo	Same	20/418	56,27	94,00	1,90	27,46	51,69	11,18
14	"	"	20/407	28,52	69,50	16,01	43,31	9,61	18,75
15	"	"	20/412	36,98	78,40	16,21	37,45	18,72	15,46
16	"	Silicical-careous rock	20/413	55,30	89,10	11,18	25,42	42,06	6,17
17	Shkapovo	Same	5/59 1141	30,08	64,60	18,18	35,16	7,74	22,24
18	"	"	5/59 1139	29,92	64,50	19,17	30,98	7,23	20,24
19	Sterlibashevo	Marl siliceous	13/677	40,95	61,80	28,40	44,24	7,22	7,57
20	Kirovskaya	Marl	4/773	39,95	77,10	14,31	25,96	21,68	20,81
21	"	Siliceous	4/775	29,31	77,10	9,71	47,01	16,48	14,89
22	Okhlebinino	Silicicalcareous rock	4/265	45,02	92,90	2,89	44,17	40,03	6,42
23	"	Same	4/268	38,50	85,80	10,43	42,99	26,42	6,58
24	Karly	Limestone siliceous	13/28 715	28,76	84,7	8,81	56,34	18,87	0,74
25	"	Limestone clayey-siliceous	13/28 716	18,45	81,80	8,56	72,55	9,65	5,57
26	Kebyachevo	Same	1/51 734	36,72	64,60	25,28	53,27	7,30	4,82
27	Karly	Limestone clayey	13/28 718	16,75	68,30	10,47	67,87	4,81	9,38
28	Akineevo	Limestone siliceous-clayey	24/668	33,93	73,00	21,67	51,96	10,87	6,96
29	Cherkassy	Limestone clayey	1/69	28,30	64,90	20,97	58,86	4,89	6,47
30	Yugomashevo	Same	20/405	18,83	79,50	10,92	60,72	8,01	12,45
31	"	Limestone siliceous	20/415	26,35	86,00	7,77	65,83	17,76	8,23
32	"	Same	20/417	23,50	94,90	3,39	65,62	20,13	7,20
Komi ASSR †									
1	Ukhtinskii region	Silicical-calcareous	7	-	40,84	13,58	20,10	32,19	18,69
2	Same	Same	65	-	38,62	12,38	39,67	30,76	9,19
3	"	"	51	-	38,38	9,87	36,68	32,14	13,25
4	"	"	14	-	48,80	15,44	15,76	39,04	16,71
5	"	"	25	-	31,16	16,90	28,26	20,40	17,15
6	"	Silicite calcareous-clayey	33	-	57,38	11,62	10,87	50,10	15,69

TABLE 1 (continued)

1	2	3	4	5	6	7	8	9	10
7	"	Silicical- careous rock	47	-	39,80	12,25	27,18	31,96	17,23
8	"	Same	140	-	39,82	7,15	43,75	35,24	6,83
9	"	Limestone siliceous	135	-	32,72	6,50	50,83	28,61	6,00
10	"	Same	6	-	21,94	3,46	69,57	19,75	3,85
11	"	Silicite	12	-	83,94	4,52	4,89	81,06	6,19
12	"	Limestone siliceous	17	-	27,96	3,46	63,05	25,77	5,32
13	"	Silicite calcareous	57	-	82,16	4,94	6,51	79,04	5,65
14	"	Same	79	-	73,48	4,53	16,43	70,59	4,90
15	"	Limestone siliceous	114	-	37,72	4,52	50,83	34,84	5,00
16	"	Silicical- careous rock	142	-	52,02	7,53	25,54	47,22	9,18
17	"	Same	152	-	47,00	5,36	38,32	43,63	7,37
18	"	"	156	-	42,00	6,02	44,02	38,16	5,31
19	"	"	175	-	40,54	5,39	44,29	37,15	6,18
20	"	"	182	-	28,28	2,89	47,28	26,47	4,80
21	"	Limestone siliceous	217	-	11,96	1,92	80,58	10,76	4,29
22	Ukhtinskii	Limestone siliceous	5	-	16,66	2,87	77,45	14,87	3,14
23	Same	Limestone	10	-	4,82	0,83	92,68	4,33	0,92
24	"	Limestone siliceous	20	-	28,78	3,43	62,15	26,62	3,98
25	"	Limestone	24	-	7,92	3,47	89,15	5,72	0,40
26	"	Same	46	-	29,98	2,88	61,83	28,18	3,57

*Analyses performed by S. A. Rossik.

†Data of S. V. Maksimov [3].

*Silicon dioxide calculated for undissolved residue.

served as the objects of study. Generalizations were drawn from the results of studies of almost 100 rock samples at the base of the Semiluksk horizon (Table 1).

A wide range of variation in the concentrations of rock-forming materials was found. Thus, clay content ranged from several percent to 67%, the content of free silica ranged from 1 to 70%, the carbonate content ranged from 0 to 95%, and C_{org} reached 30%. An increase in clay content and a decrease in the content of free silica in the north and northwestern directions is evident on a map of the region within the boundaries of the Kamsk-Kinel'sk system of basins (KKSBB), which is the primary zone of occurrence of the Domanik facies. For example, the silica content reaches 33% in the Shalym'sk basin, while the silica content usually does not exceed 4% in the basins of the KKSBB territorially adjacent to the Cis-Ural trough.

The highest (averaging 12.84%) contents of organic carbon were found in the deposits of Western Baskir. Lower content of carbonates (25.80%) in relation to high (23.94% clay content is also characteristic of these deposits. Among the samples studied, the carbonate content was high for the rocks of the Permsk Prikam'ye; the content of free silica was usually low (8.24%). The concentrations of the latter are usually high in the rocks of the Urals and Komi ASSR (41.28 and 34.41%, respectively).

No paired dependences unique for different regions were detected between the primary constituents (Table 2; Fig. 1). Only in the Southern Urals and Komi ASSR can a tendency be detected for an increase in C_{org} as carbonate content decreases and clay content increases. The correlation coefficient between C_{org} and free SiO_2 ranges from -0.55 to +0.55. A similar situation holds for the mineral components.

In order to clarify the interrelationships between all four constituents simultaneously, we used the method of major components (MC) [1, 2] allowing us to reduce the number of random quantities without substantial loss of information concerning variability. In this pro-

TABLE 2. Coefficients of Paired Correlations

Parameters X/Y	Permsk Prikam'ye				Southern Urals			
	$\bar{X}$	$\bar{Y}$	r	n	$\bar{X}$	$\bar{Y}$	r	n
C _{org} /carbonate	3.14	70.60	-0.32	16	3.80	31.76	-0.53	22
C _{org} /SiO ₂ (free)	3.14	8.24	0.26	16	3.80	41.28	0.55	22
C _{org} /clay	3.14	11.79	0.13	16	3.80	13.84	0.58	22
Carbonates/clay	70.60	11.79	-0.33	16	31.76	13.84	-0.75	22
Carbonates/SiO ₂ (free)	70.60	8.24	-0.38	16	33.84	41.28	-0.94	22

Parameters X/Y	Western Bashkiriya				Komi ASSR			
	$\bar{X}$	$\bar{Y}$	r	n	$\bar{X}$	$\bar{Y}$	r	n
C _{org} /carbonate	12.84	25.80	0.22	17	7.72	44.14	-0.66	26
C _{org} /SiO ₂ (free)	12.84	25.80	-0.55	17	7.72	34.41	0.02	26
C _{org} /clay	12.84	23.94	-0.12	17	7.72	6.68	0.93	26
Carbonates/clay	25.82	23.94	-0.57	17	44.14	6.68	-0.35	26
Carbonates/SiO ₂ (free)	25.82	25.80	-0.32	17	44.14	34.41	-0.84	26

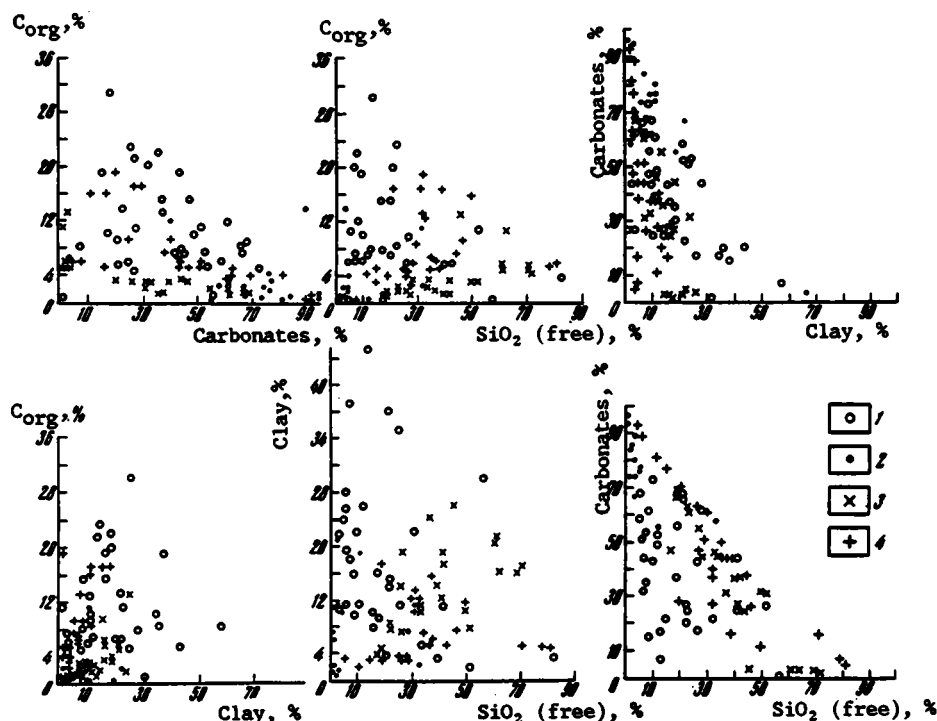


Fig. 1. Dependence between contents of primary rock constituents. 1) Western Bashkiriya; 2) Permsk Prikam'ye; 3) Southern Urals; 4) Komi ASSR.

cess, the original set was linearly transformed to a new set of independent random values arranged in order of decreasing variance. These new values are referred to as the major components. A first few major components usually account for the major portion of the total variability [2]. Calculations were carried out for all of the regions studied separately, in pairs and for a combined sampling.

As a rule, the first major component encompasses the major portion of the variability (up to 94.6%), and the second major component accounts for the remaining portion of the variability. For the Permsk region and the Southern Urals, the first major component is the degree of variability of the carbonate content in the rock. For the Ukhtinsk Region, the first major component takes into account clay content in addition to carbonate content, but much to a much smaller degree. The second major component is the total degree of variability associated with the mineral constituent of the rock; here, the carbonate content and clay con-

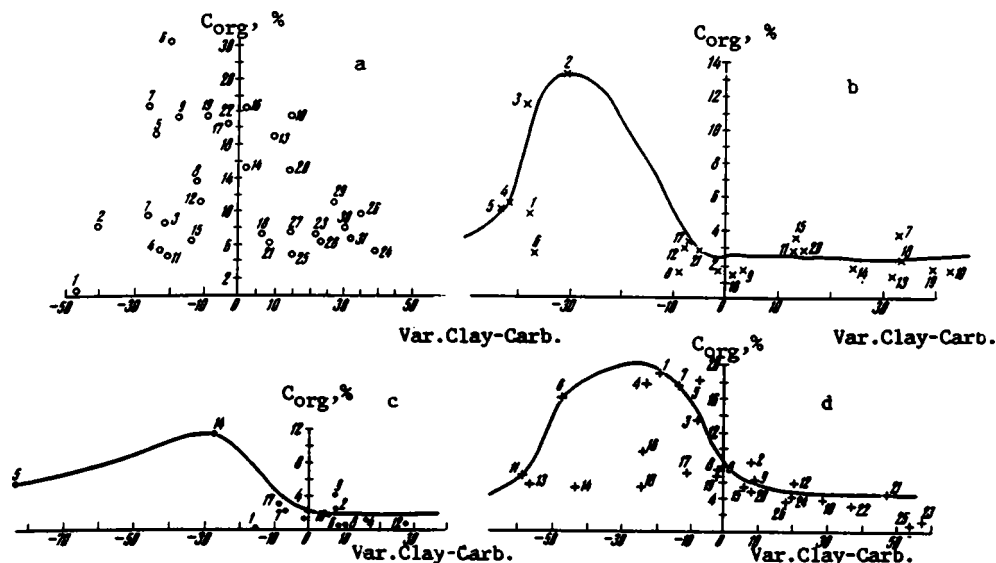


Fig. 2. Dependence of C_{org} content upon the first major component (Var. Clay-Carb.). a) Western Bashkiriya; b) Southern Urals; c) Permsk Prikam'ye; d) Komi ASSR. The numbers of the points correspond to the numeration presented in Table 1.

tent make the largest contributions to the total variability, and silica content (which, moreover always has a sign opposite that of the first two constituents) makes a much smaller contribution.

A graph of the dependence of C_{org} variation upon the first major component has a sharply expressed maximum in the region of 15-30% in the majority of cases (Fig. 2). By substituting the mineral composition of the sample at the corresponding points on the graphs, one can see that, with the exception of Western Bashkir, the points are positioned in strict correspondence with the change in carbonate content; with decreasing carbonate content, C_{org} in the rock increases smoothly and reaches some maximum value, usually for a carbonate content in the range of 15-40%; the C_{org} content then falls with further decreases in the content of carbonate. The mineral compositions of the rocks vary in different ways in this case. Thus, the clay content (from 4 to 16%) and the silica content (from 19 to 70.6%) increase simultaneously with decreasing carbonate content (from 69% to 2.3%) for samples from the Southern Urals. A rock sample with the maximum content of C_{org} (equalling 13.35%) has the following composition, in %: SiO_2 (free), 45.69%; Σ carbonates, 2.84; and clay, 26.38. For Komi ASSR, there is an increase in silica content (from 4.3 to 81.1%) simultaneous with a decrease in carbonate content (from 92.7 to 4.9%); clay content also increases in general, but reaches a maximum value (13.58 to 15.4%) coinciding with the maximum for C_{org} (16.71-18.69%) and falls again to 4.5%. The maximum (18.69%) value for C_{org} belongs to a sample with the composition, in %: SiO_2 (free), 32.19; Σ carbonates, 20.1; clay 13.58. For the Permsk Region, the opposite situation exists: clay content increases (from 0.9 to 66.6%) with decreasing carbonate content of the rock (from 96.4 to 3.6%); the silica content varies in a manner analogous to the variation in clay for the rocks of the Ukhtinsk Region, increasing from 0 to 31% and then falling. The rock samples with maximum (11.67%) content of C_{org} have a composition, in %: SiO_2 (free), 31.43; Σ carbonates, 39.51; clay 10.93. We did not detect a regular variation in composition and the content of organic carbon connected with it in the rocks of Western Bashkiriya. The major component accounted for only 54% of the total variability in this case, in contrast to 82.95% in the previous variants. While the major component encompassed the variability associated with the mineral composition of the rock in general, the clay content changed with a sign opposite to that of the carbonate content and the silica content.

From the material presented (Table 1, Figs. 1, 2), it is evident that elevated concentrations of C_{org} (more than 5%) do not coincide with a specific lithological type of rock: the range of variation of clay content, silica content, and also carbonate content in rocks with high content of C_{org} is very wide.

In general, the ratio of organic material (OM to C_{org} , $K = 1.3-1.4$) to mineral constituents is controlled by the fact that, in a four-component system (which the rocks under consideration are), the sum of all components (A) is a constant theoretically equal to 100%, but in practice, somewhat less than the sum of several undetermined components (Π):

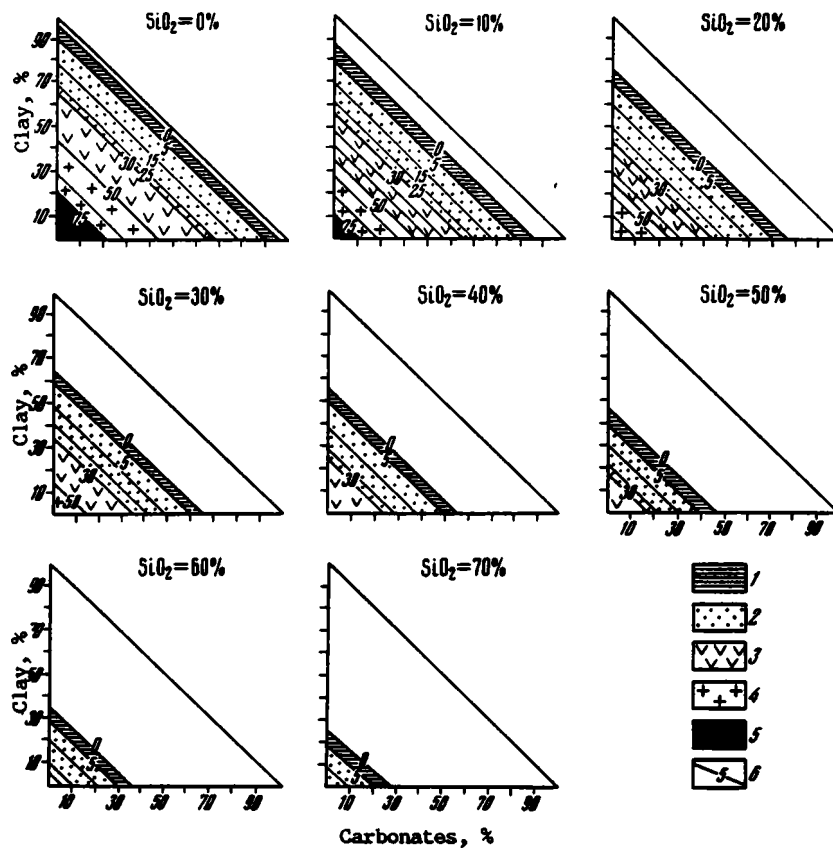


Fig. 3. Change in the concentration of OM as a function of clay content and carbonate content for fixed concentrations of free silica: 1) disseminated OM; 2) semiconcentrated OM; 3-4) shales, [3), oil, 4) carbonaceous rocks]; 5) coals; 6) isoline of equal contents of OM, %.

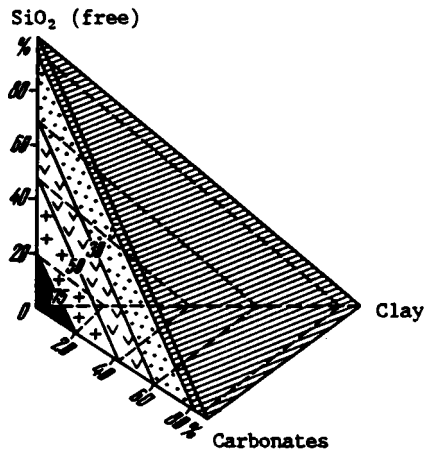


Fig. 4. Theoretical model of distribution of concentrations of primary rock constituents. For symbol designations, see Fig. 3.

$$\text{OM} + \text{Carb.} + \text{Clay} + \text{Sil.} = \text{const (A)}, \quad (1)$$

$$\text{OM} = A - (\text{Carb.} + \text{Clay} + \text{Sil.}), \quad (2)$$

$$A = 100 - \Pi$$

where Carb. represents carbonates and Sil. represents SiO_2 .

From formula (2), it is evident that an increase in the content of any component for fixed values of the others results in a decrease of OM. A simultaneous variation in the

carbonate, clay, and silica contents can take place in such a way as to not reflect substantially upon the OM. When there is a parallel decrease in all of the mineral components, the OM content increases and a transitional series of rocks from pure limestones, clays, and silica through intermediate types of rock (clayey limestones, calcareous silicites, marls, etc.) to black shales and coals can be observed.

The graphic interrelationship between the four components in the rocks (clays, carbonates, silica, and OM) is shown in Figs. 3 and 4. The model was constructed for $\Pi = 5\%$. According to our data, this corresponds to the average value of the undetermined losses. The deviation of the experimental data from the theoretical will be larger the greater the actual value of the undetermined components differs from the 5% we have assumed. The variation in OM concentration with changes in clay content and carbonate content for fixed values of silica content is shown in Fig. 3. The series of triangles in Fig. 3 are cross-sections of tetrahedrons (see Fig. 4) showing the interaction of all four primary components, actually being a graphic expression of a classification of four-component rocks with high OM content in which oil-source rocks with high concentrations of organic material, shale, and coal occupy specific positions.

Highly carbonaceous rocks are a transitional type of rock with respect to OM content, they are part-way between widely occurring oil-source rocks containing disseminated organic material to shales concentrating OM, which then becomes the major rock-forming component. Rocks of the Domanik type, just as oil-shales, do not coincide with a specific lithological type; the range of variation in their mineral composition is fairly wide. At the same time, the OM content in these deposits is significantly determined by the type of rock: the more regular the pattern of variation in the mineral composition of the rock, the more definable the character of the distribution of OM within it (for example, the Domanik deposits of the Permian Region, Southern Urals, and Komi ASSR). On the other hand, if a clear pattern of the compositional variation within the rock is not found (Western Bashkiriya), then the distribution of OM within the rock proves to be chaotic. In other words, the greater the variance of any mineral component of the rock for a constant level or a small variance of the two remaining components, the greater will be the scatter associated with the OM content in the rock; one will inevitably see a close interrelationship between OM and the maximally variable component.

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UNUSUAL TYPES OF METALLIFEROUS MINERAL DEPOSITS
IN FISH BONE DETRITUS IN MAIKOP SEDIMENTS

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UDC 553.643:551.781.5

Compositionally unusual stratified accumulations of fish bone detritus with rare-earth elements, associated with intensive sulfide mineralization and large amounts of redeposited material, such as foraminifera, glauconite, and considerable amounts of fish remains derived from Eocene and Paleocene rocks, have been identified and described.

The Maikop marine clay formation of Oligocene to lower Miocene age can be included among those unique formations that have no geological analogue. This extremely thick geological unit (up to 2 km, and in the Black Sea up to 5 km) composed primarily of clay extends for several thousand kilometers across the southern part of European USSR from the Carpathians to beyond the Caspian Sea. The unusual nature of the Maikop marine basin, which has been recognized among a number of epicontinental basins of the Platform region, has been pointed out in the literature. Among its most important features are deep basins which have not been filled with sediments, as first recognized by Stolyarov [14] in data on South Mangyshlak. It was later shown that this unique feature occurs over a broad area and is related to the development in the Paleogene, especially the early Oligocene, of deep-water basins in the area of the modern Middle Caspian and Eastern Caucasus foothills [2, 12, 16]. Sharply differentiated morphological types have been established in the Maikop marine basin, where marginal, shelf, and relatively shallow-water regions and a central basin with bathyal depths (on the order of 1000 m) have been recognized [3]. In accord with the structure of the basin marked differences in thickness and facies of the clayey deposits have been determined, and apparently the periodic contamination of bottom waters by hydrogen sulfide as well (as in the modern Black Sea). As a result, bottom fauna are poorly developed or entirely lacking, and fish remains are widespread, both scattered and as bedded deposits of fish-bone detritus accompanied by intensive sulfide mineralization [4, 6, 9, 15]. The nature of such exotic deposits, which have been studied in various areas of the Caucasus and Caspian Regions, is generally the same. They are composed of three basic components: clay (50-70%), iron sulfides (20-30%), and fish fossils (15-20%). In some deposits the fish fossil content may increase to 30-40% or more, or it may decrease to a few percent with a concomitant increase in sulfides, forming "sulfide beds" [4, 15].

Fish fossil and iron sulfide beds are of interest not only as unusual geological deposits but also as producers of large amounts of various metals. A number of chalcophile elements, including Ni, Mo, Co, Cu, Zn, Pb, and As [6], are present in quantities ranging from hundredths to tenths of a percent. The most interesting metallogenic feature of fish bone detritus is the presence in calcium phosphate of rare metals, of which the greatest amounts are rare-earth elements and yttrium (up to 0.5 to 1.0%). This is considerably more than the maximum content of rare-earth elements in chemogenic phosphates, which reaches 0.15% [7, 17].

Lithologic studies of the Maikop sequence have been very uneven. There is little information on the composition and structure of deposits in the deeply buried parts of the Western and Eastern Caucasus area. Data on the Chernykh Zemel' Region in Kalmykia, where in recent years the authors happen to have been studying Maikop deposits in a number of drill cores, are very sparse. Stratified units with metal-bearing fish bone deposits, unusual both in composition and geologic setting, have been established here; the present article is devoted to a description of these. The deposits considered here are markedly different from any known before. In addition to clay, iron sulfides, and fish fossils they contain considerable amounts of massive foraminifera and glauconite. The geological setting of these deposits is also in many respects unusual. In order to elucidate this aspect, we present some general information which has also been newly obtained in this region.

Mingeo SSSR, Moscow. Translated from *Litologiya i Poleznye Iskopaemye*, No. 1, pp. 52-65, January-February, 1989. Original article submitted March 28, 1988.

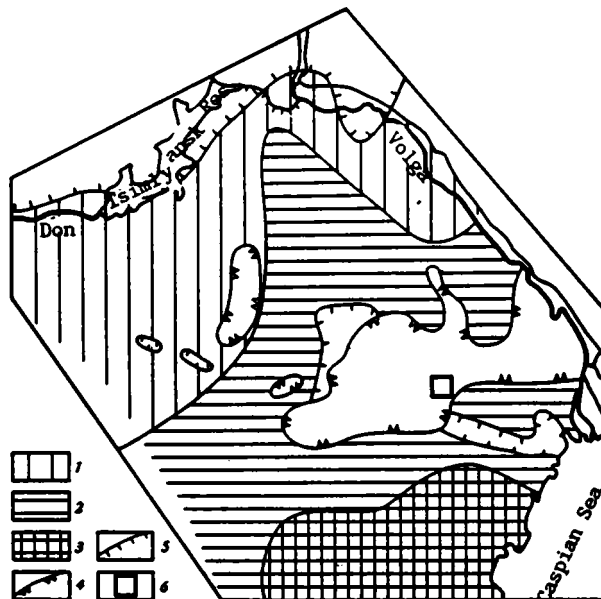


Fig. 1. Map of paleogeographic facies zonation of the Tsimlyansk suite, lower to middle Oligocene: 1) inner shelf zone (sandy-silty clays with no fish fossils); 2) outer shelf zone (calcareous clay with scattered fish fossils, with noncalcareous clay and siltstone interbeds to the northwest); 3) deepwater basin (fine-grained calcareous clay and marl with scattered fish fossils); 4) boundary of areas with no sediments of the Tsimlyansk suite (teeth on side with no sediments); 5) boundary of Neogene-Quaternary erosion (ticks on side with no sediments); 6) area of study.

Quite recently Semenov and Stolyarov [13] have presented a new interpretation of the Maikop series in the Volga-Don Region, including the Chernykh Zemel' area. Two suites are referred to the lower to middle Oligocene: Tsimlyansk (at the base), subdivided into two subsuites, and Solenovsk, composed of the ostracodal and Ikiburul'sk beds. Most of the upper Oligocene consists of the newly recognized Kalmytsk suite, the lower subsuite of which is characterized by "virgulinelli" and "fish" beds; strata with bony fish detritus of the type described above ("traditional" type) are restricted to the latter. The upper subsuite of the Kalmytsk suite, as well as the Nugrinsk suite of the upper Oligocene, are composed of clay with essentially no fish fossils. The lower Miocene part of the section is represented by the Aradyk and Tsagankhak suites in which sandy to silty clays with beds of sand and silt predominate.

The areas of the Southern Chernykh Zemel' and the Astrakhan Volga, adjacent to the Eastern Caucasus Region (Fig. 1), are characterized by anomalous features of historical geology, which are reflected in the composition and completeness of the Paleogene section, unconformably overlain by thick Pliocene deposits (Fig. 2a). Of considerable interest with respect to the geological history is the major unconformity between the Maikop section and older deposits. A number of horizons of both the Eocene and Oligocene are missing at this interformational boundary. The maximum hiatus is present where upper (Ikiburul'sk) beds of the lower and middle Oligocene overlie upper Paleocene rocks (see Fig. 2b). It is at this boundary that relict beds and lenses with bony fish deposits, glauconite, and foraminifera are found.

The deposits described below were encountered in drill holes at depths of about 500 m. They are oval in shape, and represent lenticular bodies several kilometers in length that overlie various rocks of Eocene and Paleocene age. These bodies are overlain in apparent conformity by uniform, thin (20 m) clays of the lower to middle Ikiburul'sk beds. Further

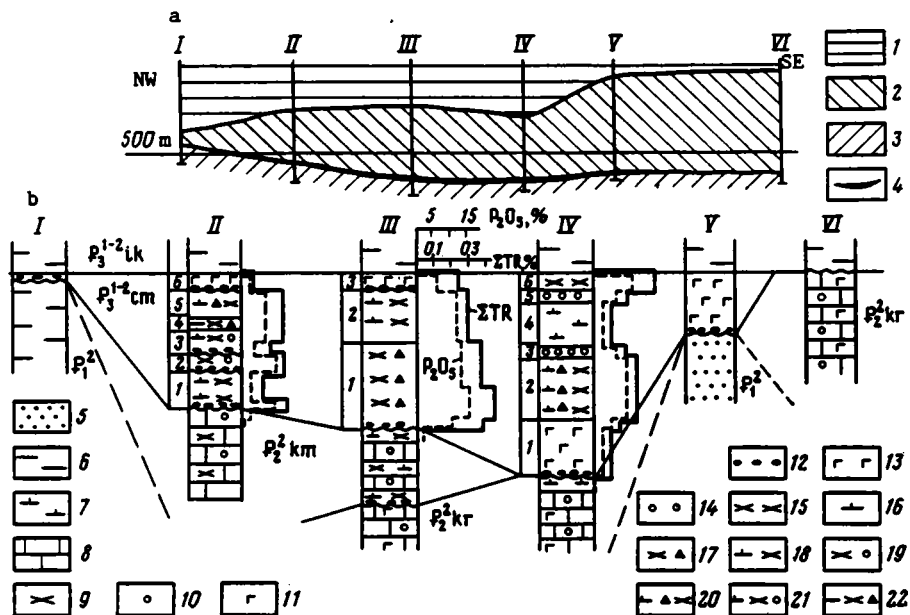


Fig. 2. Structure (a) and composition (b) of metalliferous deposits with distribution of phosphorous pentoxides and rare-earth elements in the section: 1) Pliocene deposits (calcareous clay and siltstone); 2) middle to upper Oligocene deposits (clay with scattered fish fossils); 3) middle Eocene to upper Paleocene deposits (glaucinitic sandstone, foraminiferal limestone, clay with fish fossils); 4) fossil fish bone deposits; 5) glauconitic sandstone; 6) clay; 7) same; 8) limestone. Organic and mineral content: 9) fish fossils; 10) foraminifera; 11) glauconite; 12) "bone breccia." Multicomponent rocks of the metalliferous deposits with one or more components predominant (shown on the left): 13) glauconite; 14) foraminifera; 15) fish fossils; 16) calcareous clay; 17) fish fossils with iron sulfides; 18) calcareous clay and fish fossils; 19) fish fossils and foraminifera; 20) calcareous clay, iron sulfides, and fish fossils; 21) calcareous clay, fish fossils, and foraminifera; 22) clay, fish fossils, and iron sulfides. $p_3^{1-2} lk$, Ikiburul'sk beds of the lower-middle Oligocene Solenovsk suite; $p_3^{1-2} cm$, lower-middle Oligocene Tsimlyansk suite; $p_2^2 km$, middle Eocene Kumsk suite; $p_2^2 kr$, middle Eocene Kerestinsk suite; p_1^2 , upper Paleocene. Bed number shown on left side of column.

up-section are clays with fish fossils, in the upper Oligocene Kal'mytsk suite, the base of which is clearly marked by the foraminiferal guide fossil *Virgulinella* ex gr. *pertusa* (*Virgulinella* bed). Thus the top of the section under consideration is quite well delimited. On the other hand, the age of the lower boundary is rather obscure, since the ostracodal beds and the lower to middle Oligocene Tsimlyansk suite, as well as the entire upper Eocene, are missing from the section.

The youngest rocks of the underlying complex are in the middle Eocene Kumsk suite, which is widely developed in the Caucasus and beyond the Caspian (the Shorymsk suite of Mangyshlak). Their main feature is the widespread development of scattered fish fossils and pelagic foraminifera in the limy deposits [18]. The Kumsk suite retains its lithologic character in this region. In sections II and III (see Fig. 2) it is represented by thin (0.7-2.0 m) light cream-colored foraminiferal limestones and calcareous clays with large amounts of fish fossils (scales and platy bones); locally they form lenticular deposits. The Kumsk suite contains characteristic rich foraminifera deposits with *Globigerina turcmenica*, *G. bulloides*, *G. instabilis*, and others.*

*All foraminifera identifications by G. G. Kurgalimova (PGO "Aérogeologiya").

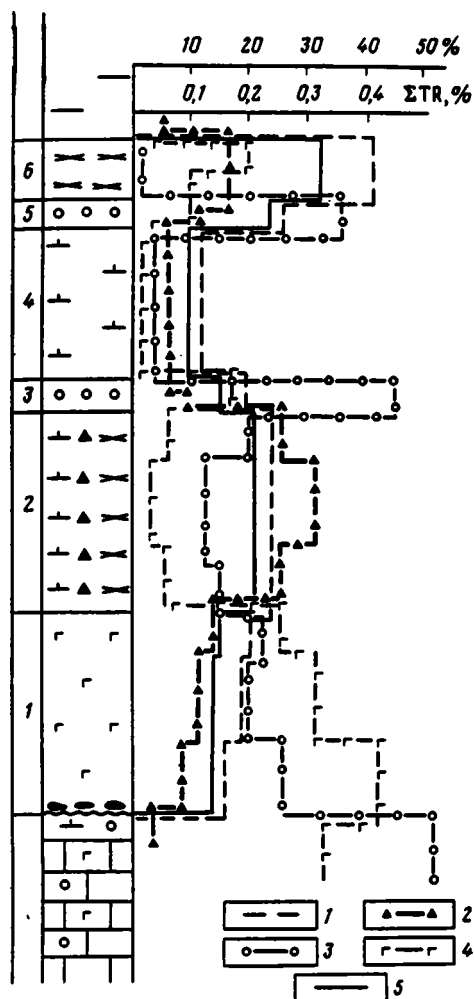


Fig. 3. Distribution of main rock-forming components and total rare-earth elements in section IV: 1) fish fossils; 2) iron sulfides; 3) foraminifera; 4) glauconite; 5) total rare-earth elements. Other symbols as in Fig. 2.

Also underlying are thin (a few meters) white foraminiferal limestones of the middle Eocene Kerestinsk suite with abundant foraminifera of various species: Globigerina eocaenica eocaenica, G. pseudoeocaenica pseudoeocaenica, Acarinina crassaformis, A. pentacamerata, Globigerinella voluta, Spiroplectammina carinatiformis, and others. Middle Eocene limestones unconformably overlie upper Paleocene clays, siltstones, and glauconitic sandstones. Foraminifera in these rocks are not very abundant, but are varied in species: Acarina acarinata, Globigerina incista, G. linaperta, Spiroplectammina spectabilis, S. cloth, and others.

The Paleogene rocks underlying the Maikop section are known to be thin and abbreviated, with unconformable contacts: the upper and lower Eocene are entirely missing, and the middle Eocene is only sporadically present. This suggests a complex history of the region during the Paleogene, leading to the formation of unusual metalliferous deposits that contain fish fossils (bones and scales), glauconite, foraminifera, iron sulfides, clayey and calcareous material, and minor mineral inclusions. The relative abundances of these rock-forming minerals within the deposits is very irregular, which outwardly produces not a striking but a substantial lithologic variation both laterally and through the section.

At the base of the metalliferous deposits nearly everywhere there is a thin (5-7 cm) basal bed of "bone breccia," consisting of irregular accumulations of bone fragments, glauconite, and foraminifera; small (1-2 cm) angular to rounded nodules of authigenic phosphorite, shark teeth, eroded clay clasts, fragments of charred wood, and rarely individual grains of quartz are found locally. It must be noted that the macroscopic perception of this basal bed as a true breccia is erroneous, and is caused by the presence of the relatively coarse (1-2 cm) bone fragments, shark teeth, and phosphorite nodules. On the basis of granulometric analysis, the conglomeratic fraction is small (up to 4%) and sand is the predominant size of the material (70%); the silty fraction is 16% and the clay-size fraction is 10%. Thus the basal bed should be called a sandstone, in which isolated coarser fragments are present.

Higher in the section it is difficult to recognize any general gradation in the beds. We therefore present a brief description of several sections that differ in composition and content (see Fig. 2). In the thickest (2.4 m) section, section IV (Fig. 3), the lower part (bed 1; 0.7 m) is dark green in color due to the predominance of glauconite grains (32%); it also contains lesser amounts of bony detritus (18%), foraminifera (22%), iron sulfides (12%), and clayey-carbonate material (26%). The rock is obscurely lenticular-bedded. Sand-size grains predominate (68%), silt and clay are about the same (about 16%), and gravel is no more than 2%.

In the middle of the section (bed 2; 0.75 m) the proportion of rock-forming components decreases markedly. There is more clayey material (30-32%), iron sulfides (up to 30%), and fish fossils (24%); foraminifera (12-20%) and especially glauconite (3-6%) have decreased in amount. The bony detritus is relatively evenly distributed, while the sulfides are mainly dispersed ("sooty") throughout the clayey material, locally forming small clusters of finely crystalline pyrite and marcasite. Bedding is poorly developed, and is seen in individual more intensive accumulations of bony fish detritus, foraminifera tests, or glauconite grains. The grain size distribution is as follows: sand, 42%; silt, 25%; clay, 32%; coarser material (1+ mm), less than 1%.

Higher in the section is the thin (0.1 m) bed 3, clearly delineated by foraminifera (up to 40-45%), with accumulations of glauconite (15-20%) and fish fossils (20%); there are considerably less sulfides (up to 10%). Because of the large amount of foraminifera the sand fraction increases to 70% and gravel to 3%; silt and clay fractions are reduced in size (12-15%). The succeeding bed 4 (0.55 m) is composed mainly of clay (70-75%) and dark-gray limestone with a decreased amount of fish fossils, glauconite, and foraminifera, which occur separately in the rock. Above this (bed 5, 0.1 m) is another major concentration of foraminifera (up to 35%); iron sulfides are considerably reduced (12%) and glauconite occurs as individual dark-green grains. The presence of large foraminifera causes an increase in the fraction 1+ mm (about 6%); the sand fraction is smaller (43%) and the silt larger (31%) than in bed 3.

The uppermost part of the section (bed 6; 0.2 m) is distinguished by a higher concentration (up to 40%) of fish fossils; at the contact with the overlying unit there are many dark-green grains of glauconite, and the sulfide content reaches 17%. It should be noted that the grain-size distribution is much finer here: sand 22%, silt 47%, and clay 31%.

The average content of the main components in the whole unit in the section given (2.4 m) is: fish fossils, 25%; iron sulfides, 17%; glauconite, 18%; foraminifera, 20%; carbonate-clay cement, 21%. The average grain size: gravel, 2%; sand, 55%; silt, 22%; clay, 21%. The rock should thus be termed a carbonate-clay-cemented siltstone.

No predominance of any one component is seen on averaging the composition. The five components of the metalliferous rock are approximately equivalent. In actuality, however, as indicated by the bed-by-bed description, the proportion of the components varies. Some patterns can be distinguished (see Fig. 3). For example, there is commonly a direct relationship between fish fossils and iron sulfides; this may also be true for glauconite and foraminifera (with some exceptions). Moreover, these two sets of components show a more or less clearly defined inverse relationship with each other. The authors will examine the genetic implications of this phenomenon in future studies.

The deposits are not as thick (1.8 m) in section III. The lithologic (and stratigraphic?) analogue of bed 1 in section IV, which is enriched in glauconite and foraminifera, is missing. At the base (bed 1; 1.0 m) are whitish to dark-gray rocks containing a large amount of fish fossils (36-45%) and iron sulfides (16-20%); grains of glauconite and foraminifera tests are seen with the unaided eye as white specks. In thin section, along with bony detritus there are local concentrations of foraminifera or glauconite grains, but often these are completely lacking. This rock is similar in composition to bed 2 in section IV, but differs in a higher content of fish fossils.

In the upper part of the section (0.8 m) the amount of fish fossils decreases to 33%, and at the top (bed 3) to 14%. In bed 2 (0.6 m) a large amount of fish scales and light-brown platy bones are found in dark-gray clayey material interbedded with concentrations of foraminifera tests (white variety) or dark-green glauconite grains. The top of the section is the greenish bed 3 (0.2 m) with a large amount of dark green (to black) glauconite (as much as 60-70% in some beds). Very large (to 0.5-1.0 cm) fish vertebrae are found, as well as shark

teeth; small phosphorite nodules and phosphatized coprolites are also seen. This bed is poorly sorted with an undulating base with traces of erosion.

The sediments in section III are distinguished by a generally very high content of fish fossils (about 35%) with a somewhat reduced sulfide content (13%).

There is considerably more lithologic differentiation in section II. At the base, above the basal "bone breccia" bed, dark-gray calcareous clay (bed 1; 0.45 m) contains laminae with a relatively small amount of fish fossils (11%). Numerous foraminifera tests are present with the fish fossils, but glauconite is almost completely absent. The amount of fish fossils increases in bed 2 (0.2 m) to 30%, foraminifera are also abundant, and glauconite appears as individual grains; there is a thin (4 cm) bed of "bone breccia" at the base with phosphorite nodules and aggregates of glauconite grains.

Above this (bed 3; 0.35 m) is a dark-gray, calcareous clay that is thin-bedded due to layers of fish fossils (20%); foraminifera tests form large whitish specks, but there is little glauconite. The fish fossils are dominated by flat, platy bones. Iron sulfides frequently occur in the form of finely crystalline pyrite nodules. Glauconite accumulations and coarser (up to 5 cm) fish vertebrae are found at the base of bed 3. The thin (0.1 m) overlying bed 4 is composed of dark-gray calcareous clay with fish fossils (20%) and iron sulfides (21%), but no foraminifera or glauconite. This rock appears to be lithologically similar to typical upper Oligocene fish formations.

Bed 5 (0.35 m), in the upper part of the section, is dark, almost black, because of the large amount (28%) of dispersed ("sooty") sulfides impregnating the clayey cement. Locally found among the fish fossils (24%), however, are light (pearly) bone fragments, which form accumulations along bedding; foraminifera are essentially absent and glauconite appears only as individual grains. The top of the section (bed 6; 0.2 m) is a glauconitic sandstone (up to 40-45%) with a relatively small amount of fish fossils and iron sulfides (about 8-10%); individual grains of quartz (1-2 mm) and fragments of charred wood are present. There are essentially no foraminifera. Rhombohedra of dolomite are seen in thin section. The rock is poorly sorted; the abundance of glauconite imparts a green to dark green color.

The average fish fossil content over the entire thickness of the deposit (1.65 m) in this section is 22 to 23%, and the average for iron sulfides is 16%.

The relationship between the main components of the metalliferous deposits in sections II and III is, as can be seen, very complex and varied. In section III, which has the most fish fossils, foraminifera and glauconite are generally reduced in amount. In certain beds in section II that are enriched in fish fossils and iron sulfides, foraminifera and glauconite are also practically absent. At the same time, higher beds in both sections are greatly enriched in glauconite while fish fossils and sulfides are reduced and there are very few foraminifera. Thus, there is some "antagonism" between the pairs "fish fossils - iron sulfides" on the one hand and "glauconite-foraminifera" on the other. Foraminifera often form concentrations together with fish fossils, but are virtually absent (as a rock-forming component) in glauconitic sandstones. This suggests a quite complex and variable environment of deposition of the metalliferous deposits both through time and within the limits of the space occupied by the deposits. For example, some subsidence can be detected in marginal areas.

We will briefly describe the basic rock-forming components. Fish fossils are the most exotic. Predominant among these are bone fragments and integuments, crushed to sand and silt sizes, and less commonly scales and coarse vertebrae, as well as shark teeth. Two basic kinds of fish fossils can be found: 1) light-colored (pearly) platy bones and scales, and 2) dark angular fragments of skeletons and fins. Often they form isolated concentrations, but they are found throughout.

Associated with the phosphatic material of the fish fossils (P_2O_5 in mineralized bones reaches 31-32%) are rare-earth elements and yttrium. The content of these in the whole rock ranges from 0.1 to 0.42%, depending on the amount of fish fossils. The correlation between phosphorous pentoxide and rare-earth elements is always clear and direct (see Fig. 2, 3). In pure ("bone") concentrates of fish fossils the rare-earth element content is higher (0.7% or more). Thus, the content of yttrium in the fraction $-0.5+0.1$ mm in bone concentrate is 0.2-0.27% and that of ytterbium, 0.01-0.014%. It should be noted that the amount of rare-earth elements in fish fossils varies within a very small range. This is indicated by the consistency of the ratio of rare-earths to phosphorous ($\Sigma TR/P_2O_5$) within the limits 0.022-0.026.

Determination of the composition of the rare-earth elements shows a strong predominance of lanthanum, cerium, and yttrium, which are present in approximately equal amounts ($n \cdot 10^{-2}\%$); the content of the remaining elements (praseodymium, neodymium, samarium, europium, gadolinium, dysprosium, holmium, erbium, thulium, ytterbium, and lutecium) is significantly lower (by an order of magnitude or more).

Sulfides are predominantly dispersed (cryptocrystalline, "sooty"), less commonly form nodules of finely crystalline pyrite and sometimes marcasite. Chalcophile elements (nickel, cobalt, molybdenum) are concentrated in the sulfide material in tenths and hundredths of a percent (over the whole rock). The content of these elements in sulfide concentrate is several times greater.

The glauconite is told mainly by color, from light green to dark green, almost black. The grains are usually rounded (abraded), but sometimes broken ("earthy"). Chemical analyses of all kinds of glauconite did not reveal any substantial differences in composition. The composition of glauconite, based on eight analyses, is as follows, %: Na_2O , 0.11-0.12; MgO , 3.71-4.13; Al_2O_3 , 9.78-10.52; SiO_2 , 47.7-50.3; P_2O_5 , 0.26-0.49; K_2O , 8.19-9.02; CaO , 0.55-1.07; TiO_2 , 0.2-0.25; MnO , 0.02-0.03; Fe_2O_3 , 18.84-20.32; ign. loss, 5.7-7.1.

Clayey material is mostly hydromica of the muscovite type, and to a lesser extent chlorite and montmorillonite. Carbonate in clayey material is pelitomorphous and is calcite or less commonly dolomite. Mineralogical impurities include feldspar and quartz (mostly the latter), as well as carbonaceous residues and phosphorite nodules.

Foraminifera tests are one of the main rock-forming components. They are obviously of interest not only in a genetic sense, as indicators of conditions of formation of the deposits, but also from the viewpoint of age determination. Detailed bed-by-bed studies of the vertical distribution of foraminifera, carried out by G. G. Kurgalimova on material supplied by the authors, revealed no differentiation of the abundant micropaleontological material. A mixture of species of different ages, in the stratigraphic range from lower Eocene to lower-middle Oligocene inclusive, was found throughout, with an overwhelming preponderance of Eocene forms, both in species and in quantity. The Eocene tests are, as a rule, abraded and sometimes deformed. Oligocene forms are distinguished by far better preservation (essentially not abraded). Found among these were species characteristic of the Tsimlyansk suite: Globigerina officinalis, G. ouachitaensis ciperensis, G. angustumbilicata, Baggina iphigenia, Valvulineria cubanica, Caucasina schischinskyae, Bolivina mississippiensis, Globorotalia permica, and others. Upper Eocene forms are an assemblage of the zone Globigerapsis tropicalis, and the middle Eocene, a mixed assemblage of the zones Acarinia bullbrooki and A. rotundimarginata; Globorotalia aragonensis is found among the lower Eocene forms. It must be emphasized that Oligocene forms are found in the lowest beds of the metalliferous deposits, while Eocene forms are also found mainly in the overlying deposits of the Ikiburul'sk beds of the Solenovsk suite of the lower to middle Oligocene. The important conclusion follows from this that these formations are stratigraphically analogous to the Oligocene Tsimlyansk suite, and the Eocene foraminifera are products of the erosion and redeposition of older Paleogene beds during early Oligocene time. We note that in the adjacent areas of Chernykh Zemel' and the Eastern Caucasus (see Fig. 1) the Tsimlyansk suite is composed of fine calcareous clays of the deep-water type, which are relatively thin (10-20 m) and have scattered fish fossils and planktonic foraminifera assemblages with Globigerina officinalis [13].

Thus, one of the main features of the metalliferous deposits is the presence of redeposited material from the erosion of earlier formed deposits. A definitive indicator of this process is the massive accumulation of Eocene foraminifera in deposits referred to the lower horizons of the Oligocene. Another anomalous component is glauconite. Its actual source may also be older rocks of Paleogene age, where glauconite is abundant and is similar in character to that in the deposits under study. It is therefore suggested that the glauconite is also redeposited. This is supported by the rounding and abrading of the grains, their concentration along with tests of foraminifera, and the envelopment of the glauconite grains in fine bone detritus, as seen in thin section (Fig. 4).

The nature of the fish fossils is more indefinite. It is apparent that a significant proportion are redeposited from the middle Eocene Kumsk suite, which in this region contains abundant fish fossils having a platy form and light (pearly) color. Such bone material is often found in the deposits under study, forming interbeds with foraminifera and glauconite. All of this would seem to point to the conclusion that the origin of these multicomponent deposits is the result of the erosion of Eocene and Paleocene rocks that contained an abundance

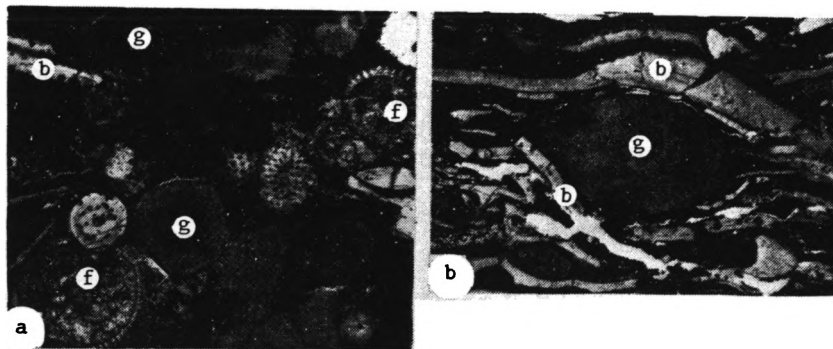


Fig. 4. Examples of the arrangement of basic components. a) Concentration of glauconite grains (g) and foraminifera (f); b) glauconite grain enveloped in bone detritus (b); black, dispersed ("sooty") iron sulfides. Plane light, $\times 63$.

of foraminifera, glauconite, and fish fossils, followed by the local redeposition of these materials.

Not everything can be explained in this way, however. Along with obviously redeposited material are fish fossils many of which are more likely of Oligocene age. These include dark, angular (skeletal) fossils having an "Oligocene aspect." But the main thing which suggests the introduction of "fresh" fish fossil material is the intensive appearance of authigenic sulfide mineralization related to sulfate reduction processes, which requires a large amount of organic material, generally supplied by a massive die-off of fish [6]. This condition is not in accord with the clean, redeposited nature of the fish fossils, already beyond the stage of diagenetic alteration and without any capacity for chemical reaction.

The appearance in the early Oligocene of processes of accumulation of fish fossils in the sediments is supported by the widespread development in adjacent areas of the so-called "fish facies" (clayey deposits with scattered fish fossils and platy organic material of animal origin, etc.), and also by the presence in the metalliferous deposits of fragments of charred wood, phosphatized coprolites, phosphorite nodules, and other features that are generally found in fish fossil beds [6, 15]. Consequently, the facies and paleogeographic conditions in the early Oligocene were favorable for the generation of "fresh" fish fossil material, although this process was complicated by the introduction and accumulation of additional, redeposited bone material, and especially glauconite and foraminifera. This circumstance places these metalliferous deposits in the class of anomalous deposits among such formations.

We will now consider the question of the concentration of rare-earth elements in fish fossils. This process is known to be quite widespread and has been found in deposits of very different ages, from Paleozoic to Recent [1, 5], including middle Eocene fish fossils. The rare-earth elements are present in a wide variety of facies, both marine and continental, and in all kinds of deposits (dispersed or bedded). Therefore, the redeposited fish fossils in the deposits under study could have already been metalliferous. The process of accumulation of rare-earth elements no doubt took place in the Oligocene as well, but apparently only in "fresh" material. As previously indicated, at the present time no differences in the concentration of rare-earth elements in mineralized fish material has been established. This is firmly supported by the persistence (at about 0.024) of the rare-earth to phosphorous ratio in bone beds of very different types. It is not clear why rare-earth elements should be the same in fish fossils of different origins. It can only be noted that in bedded accumulations in the upper Oligocene which contain no glauconite or foraminifera, the rare-earth element concentration in phosphatic fish fossils is usually higher ($\Sigma \text{TR}/\text{P}_2\text{O}_5 = 0.04$ to 0.06). Consequently, the conditions for accumulation of rare-earth elements in redeposited material apparently was on the whole, less favorable.

In what facies environment could the metalliferous formations under study have formed? Not being able to analyze this problem as a whole, since it is in many respects not yet worked out, we can only point out that the fish bone detritus in the Maikop marine basin was formed at the outer margin of the shelf zone, composed of low island chains and shoals

(banks) that were quite closely connected to depressed, deep-water basins. In such regions there was a large concentration of fish which periodically died in large quantities and were buried in sediments [6, 9, 15].

In the early Oligocene, the region under consideration was also located on the outer part of a broad shelf near a deep-water basin of the Eastern Caucasus, a considerable distance (150 to 200 km) from the shallow-water, near-shore zone of the Moscow basin (see Fig. 1). As noted above, the region of Chernykh Zemel' and the Astrakhan Volga area is characterized by a complex geologic history during the Paleogene, which is related to the appearance of large-scale positive structures by Paleocene time [18]. Notable features of early Oligocene history include the development of a broad area of "null sedimentation," which led to the disappearance from the section of the Tsimlyansk suite and ostracodal beds of the Solenovsk suite of lower to middle Oligocene (see Figs. 1, 2). The occurrence of elevated areas of the sea floor such as shoals (banks) and low island chains can be assumed. In such an environment, during the early Oligocene there was erosion of Eocene and Paleocene sediments from higher parts of the sea floor, near wave base [15], for long periods of time, with very slow accumulation of the coarse erosion products in nearby low areas. Thus, most erosion is found at the periphery of the deposits.

It is assumed that concentrations of fish near the islands periodically died in large quantities, i.e., provided "fresh" fish fossil material, organic matter, wood fragments, etc., and that they accumulated along with redeposited fish fossils, glauconite, and foraminifera. In this manner it is possible to explain the origin of such an unusual composition ("combined") of sedimentary-diagenetic formations in the early Oligocene in relatively deep-water open marine conditions.

Thus, the development of a broad area of "null sedimentation" should be considered one of sedimentary features leading to the formation of the deposits studied. The existence of such an area in the Maikop marine basin, in the South Mangyshlak region, has been noted in [10, 14, 15]. A connection between this area and a thin (0.1-0.2 m) but very persistent (up to 100-200 km) sulfide bed with fish fossils and wood fragments in upper Eocene deposits has been found [15]. Somehow in this same area thicker deposits of fish bone detritus were formed. However, the appearance of areas of erosion and nearby accumulation of redeposited material from the underlying unit is unknown in regions of "null sedimentation" (except for isolated clay galls at the margins of minor erosion).

The development of areas of decreased and "null" sedimentation in the Maikop marine basin is associated with fluctuations, sometimes quite sharply expressed, in the thickness of individual beds that locally reach several hundred meters [10, 14, 15]. In such cases the clays do not show any significant lithologic variations. Such drops in thickness, with pinchout of a number of stratigraphic units, are one of the causes of the wedge-shaped structure of the Maikop sequence, which is best shown by seismic profiling of units with sands and silts [8].

Finally, one other aspect of the occurrence under consideration should be mentioned. The development of areas of "null sedimentation" and submarine erosion is closely associated with an understanding of the origin of unconformities in the Maikop deposits, including the boundary between the Eocene and Oligocene. An unconformity at the base of the Maikop series has been established in many parts of the Caucasus and Volga-Don regions [11, 13]. It varies in stratigraphic significance. The unconformity considered in this paper is one of the most stratigraphically profound. Lower beds of the Oligocene are often found to overlies different horizons of the middle and upper Eocene.

We would like to dwell on this point for a moment. Onishchenko [11] has published a number of papers presenting a forcefully expressed view to the effect that the unconformity at the boundary of the Eocene and Oligocene is related to a regional unconformity. He emphasizes that "a broad array of data from both sides of the Caucasus indicates that the lower Oligocene is everywhere transgressive on the underlying beds ..." [11, p. 86]. In our view, Onishchenko's idea hardly requires much analysis. It is unsubstantiated inasmuch as having examined examples of the base of the Oligocene as reported in the literature, which characterize different structures or individual areas, the author quite arbitrarily refers them all to one universal effect ("everywhere transgressive"). Actually, the Eocene-Oligocene boundary in the Caucasus and adjacent regions of the Volga-Don and Caspian is mainly conformable. A prime example of this is the parastratotypic Paleogene section along the Kuban' River, where not one of the many investigators has indicated the presence of a stratigraphic unconformity

(not to mention a regional unconformity) between the upper Eocene marls and Oligocene clays.

Recent studies by the authors in the Caucasus foothills and the Volga-Don area, including project No. 174 of the International Geologic Correlation Program (IGCO), devoted to events at the Eocene-Oligocene boundary, showed that no material regression took place in this area, even in the interior zone of the shelf region of the Moscow basin. Therefore, the radical tectonism at the end of the Eocene to the beginning of the Oligocene in certain facies zones, in which stratigraphic unconformities appear, took place entirely in the Moscow basin, mainly in submarine environments. This is supported by the information presented in this paper.

We are not as yet aware of a reliable case of subaerial erosion on the island chains that existed in the outer shelf zone, where conditions for preservation of such features is less favorable.

* * *

Information presented in this paper illuminates an array of interrelated phenomena that relatively rarely occur in nature. This refers mainly to such unique formations as bedded continental metalliferous fish bone detritus and iron sulfides, which are not known outside of the Maikop clayey deposits on such a scale, i.e., they have no geologic analogue. Sedimentary-diagenetic formations with redeposited fish fossils, glauconite, and foraminifera, another very unusual occurrence, have been described for the first time. All of these exotic formations are related to areas of "null sedimentation," examples of which are also quite rare. Such areas in the Maikop marine basin, as we have shown, were formed in open parts of the basin at depths close to wave base [15].

The metalliferous deposits examined in this paper suggest that areas of "null sedimentation" do not occur only as regions where sedimentation is practically nonexistent over long periods of time. Minor erosion and local redeposition are also known to take place in these areas. In other words, areas of "null sedimentation" may be to some degree morphologically differentiated, with local "sedimentation traps" virtually isolated from the regional source of terrigenous material.

Finally, it should also be noted that the presence of unconformities in the Maikop deposits is related not only, and even not so much, to post-sedimentation erosion, but also largely to the development of areas of "null sedimentation." The large unconformity at the base of the Maikop series is apparently due to a combination of these processes. The interpretation of the nature of unconformities thus does not lead one away from an analysis of specific facies and paleogeographic conditions of sedimentation.

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SUBSTITUTION AND DEPLETION ZONES OF POTASH AND POTASSIUM-MAGNESIUM SALT DEPOSITS

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UDC 553.632.550.4

The geologic structure of substitution and depletion zones is studied for potash salt deposits in various parts of the world. The lithologic features of various types of potash-bearing formations are described. The development settings of these zones are characterized; the data suggest that they are of various origins.

Substitution and depletion zones in potash deposits often create problems for potash mining enterprises. There are many such zones in operational deposits. Studying them to reveal their formation conditions and the possibility of predicting their location and geometry is essential for geologists working in this field.

Unfortunately, these zones are often found only during the course of development of a deposit. Their unpredictability confounds deposit development planning and mining. They may not even be discovered during site surveying and quite often mine geologists learn about such zones only after preparation and operation workings are put in place. They cannot be blamed for oversight, because substitution zones are often too small for even surveying exploration to guarantee reliable discovery. After years of study we have not yet obtained to an unequivocal description of the formation settings of such zones, necessary for predictions.

Substitution and depletion zones of potash and potash-magnesium salt deposits were first discovered near the century turn in Zechstein beds in Germany. After almost a hundred years of intense studies, we now know that these zones are widespread and that their size, shape, and mineral composition vary widely. Tectonic or paleogeographic determination of the substitution zones is often unclear. As a result, the same data have been interpreted differently by different geologists. A substitution zone can be attributed to sedimentary or early diagenetic and postsedimentation processes. The latter often are associated with tectonics, and these zones are attributed to the effects of rising and, less often, sinking brines. It has been clearly established only that specific types of potash-bearing formations are characterized by specific successions of mineral composition of rocks in such zones.

At present, five cycles (series) of deposits are identified in the Zechstein halogenous formation in Western Europe, which covers an immense territory (bottom to top): Z1 (Werra),

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TABLE 1

Mineral	Carnallite rock	Hartsalz			Rock salt
		Kieserite-sylvinite	Kieserite-polyhalite-sylvinite	Langbeinite-polyhalite-sylvinite	
Carnallite	52.0	3.5	1.6	0.3	0.6
Sylvine	—	28.9	22.9	19.7	1.5
Polyhalite	—	3.1	10.1	9.1	0.7
Langbeinite	—	—	1.0	17.7	0.6
Kieserite	12.0	18.8	14.4	6.9	2.4
Anhydrite	1.8	2.5	2.1	0.4	1.4

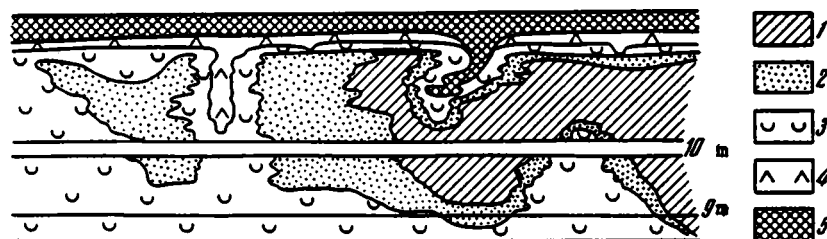


Fig. 1. Replacement and depletion of the Stassfurt bed in potash region of South Hartz (GDR) [27]: 1) carnallite rock; 2) hartsalz; 3) depleted potash bed; 4) compact anhydrite; 5) gray salt-bearing clay (9 and 10 m — marking halite interlayers).

Z2 (Stassfurt), Z3 (Leine), Z4 (Aller), and Z5 (Ore). Each cycle consists (bottom to top) of terrigenous, carbonate, anhydrite, and halite (rock salt with potash-magnesium salt layers) rocks and are covered by anhydrides. The Werra series is represented by Thuringen and Hessen potash beds; the Stassfurt series by the Stassfurt bed, the Leine series by the Ronnenberg and Riedel beds (and locally by Bergmanssegen and Albert beds), and the Aller series by portions of the Ottosshall bed.

Werra potash beds and their depletion zones have been explored in detail in the Werra-Fulda area, where there are more than 20 potash mines, with a large number of bore holes. In the Thuringen and Hessen potash beds, kieserite-containing carnallite rock is replaced by carnallitic and sylvinitic hartsalz, and then by kieserite-containing halitic rock. In case of an incomplete substitution of beds, the bottom portions of hartsalz contain more kieserite and the top portions more sylvine. In the marginal areas of the depletion zones, langbeinite and then polyhalite appear. The zones of bed depletion of rock salt are usually associated with faults, often expressed as arched rises or anticlinal folds [26]. Where the beds consist of a carnallite rock they are thicker than where hartsalz is predominant.

Some investigators [45] have interpreted carnallite and hartsalz formations as primary sedimentary or early diagenetic zonality. They view hartsalz as a facies of basin margins or shallow sea rises. Even these authors, however, attribute zones of total depletion of potash beds to tectonically weakened zones and penetration of brines through them, and sometimes also to basalt intrusions [30].

The Hessen bed is sometimes described as affected by sinking brines, where the top portion of carnallitic rock is replaced by blue or purple sylvinite [45]. Such a depletion often corresponds to sagging depressions on the day surface, stretching parallel to the depletion zones in a northeasterly Hercynian direction, similar to disruptions of Werra folding [46].

Where the Hessen bed is depleted and hartsalz is replaced by rock salt, the base of the rock salt layer contains nests and thin interlayers of kainite, astrachanite, glaserite, kieserite, and langbeinite. Halite and sulfate minerals bear traces of recrystallization, dissolution, and other secondary processes [1].

In the Soviet Baltic region, the potash horizon of the Werra series, discovered in the Niven depression, consists of sylvine-kieserite hartsalz and kainitic and kieserite-poly-

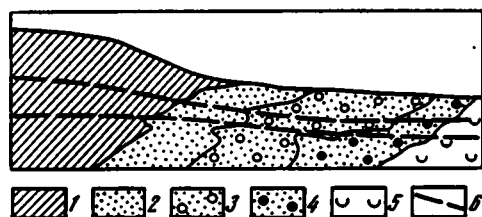


Fig. 2

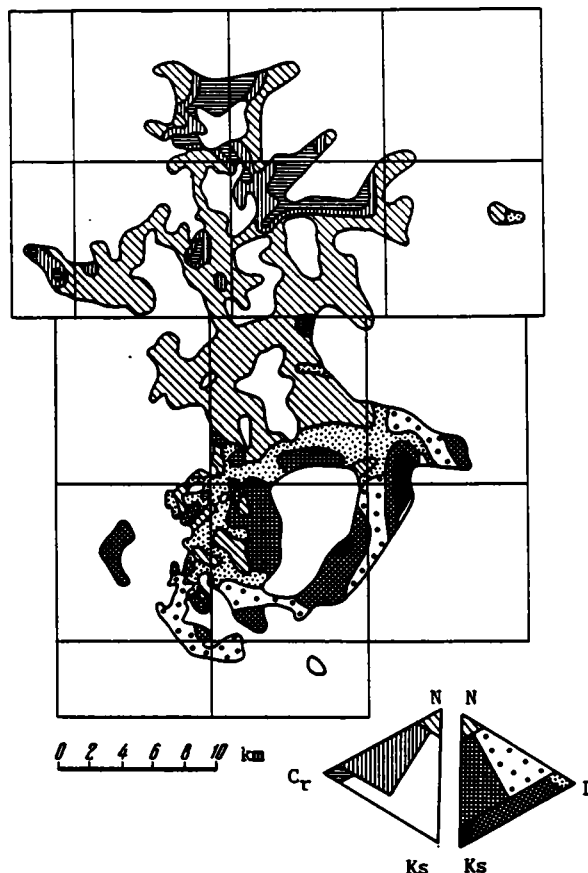


Fig. 3

Fig. 2. Variation of the mineral composition of rocks (wt.%) of Stassfurt bed in North Hartz and Saale-Unstrut (GDR) [4]: 1) carnallite rock; 2) kieserite-sylvinite hartsalz; 3) polyhalite-kieserite-sylvinite hartsalz; 4) polyhalite-langbeinite-sylvinite hartsalz; 5) rock salt; 6) rock salt maker interlayers.

Fig. 3. Lithologic-facies zones, fifth ore section, potash salt deposit, Carlsbad (US) [37]. Symbols at corners of mineral composition diagrams: Cr = carnallite; S = sylvine; Ks = kieserite or kainite; L = langbeinite, leonite, schoenite, astrachanite, vanthoffite, glaserite, and loeweite.

halitic rocks [15]. Hartsalz and the kainitic rock in the peripheral parts of the bed may have experienced postsedimentary polyhalitization as a result of substitution processes.

Stratigraphic equivalents of this horizon, discovered by drilling north of Gdansk on the Leba upland in Poland may also be products of this process; they consist of thin layers of a polyhalitic rock and carnallite, kainite, glaserite, and loeweite inclusions [14].

The Stassfurt potash salt bed is widespread almost over the entire Middle European trough and in central parts of certain side depressions, where it is more accessible and has been studied in more detail. In the north German, northeast German, and Altmark depressions of the Middle European trough, where the bed occurs at a great depth, it consists mainly of carnallitic rock. In the side depressions (Thuringen, Subhercynian, and Weserian), the Stassfurt bed exhibits two types of sections: carnallitic and hartsalz. On some areas it consists almost entirely (or mainly) of kieserite-carnallite rock. Hartsalz sections consist of sylvinite, kieserite, langbeinite, kainite, and loeweite rocks; in addition, there is glauberite and anhydrite at the bottom.

In the Stassfurt potash-bearing region, the Stassfurt bed, consisting of a carnallitic rock, is thicker than where it is hartsalz. Carnallitic rock is detrital, partly laminated at the top. In transition zones it is gradually succeeded by hartsalz from bottom to top, member after member. Sylvinitic hartsalz gives way to langbeinitic and kieseritic varieties

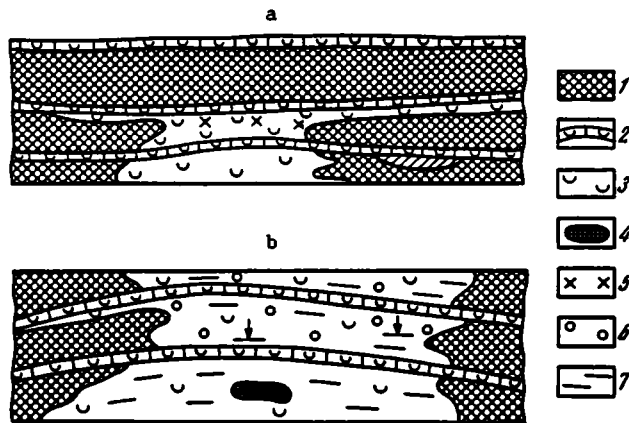


Fig. 4. Depletion zones in the first ore section of the Carlsbad deposit (US) [39] (a - depletion of lower and middle sylvinite layers, b - depletion of all three sylvinite layers): 1) sylvinite; 2) marker layers of orange halite; 3) rock salt; 4) lenses of recrystallized milk-white sylvine; 5) sylvinite insets; 6) polyhalite inclusions; 7) clay interlayers (arrows mark brown clay).

and, finally, is replaced by a halitic rock of the depletion zone [47, 48]. The carnallite rock is the only one believed by all investigators to be a primary sedimentary formation, even though it has been fractured with disruption of layering. As to hartsalz, its genesis has been interpreted as: 1) primary sedimentary; 2) early diagenetic; 3) secondary epigenetic and prototectonic; 4) secondary epigenetic and synposttectonic; and 5) secondary epigenetic and posthumous [40]. Ironically, different interpretations are often "supported" by the same facts. The sharp transitions of carnallite rock to hartsalz, the stassfurgite (boracite) nodules with a carnallite kernel found in hartsalz of marginal depletion zones and finds of langbeinite, kainite, tachhydrite, and fibrous carnallite in hartsalz, neomorphs of secondary sylvinite, and blue halite in the transition zone, where the bed is often folded - all seem to be likely signs of a metasomatic alteration of carnallitic rock to hartsalz under the effect of rising sulfate-containing chloride brines [47]. Yet, some investigators believe that hartsalz in this region can be of a dual genesis [40]. It experienced most profound change in the northern and southern Harz (Figs. 1 and 2; Table 1), where it is sometimes even represented by anhydritic hartsalz. The fact that hartsalz is confined to marginal bed facies and Hercynian-oriented arch rises is insufficient for deciphering its genesis unequivocally. The increased thickness of overlying gray salt-bearing clays and linear rock salt of the Leine series and red salt-bearing Aller clays discovered over depletion zones [46] documents that the sagging zone belongs to the Zechstein time. This probably indicates an early diagenetic hartsalz formation. Interstratification of carnallite rock with hartsalz, with locally preserved layering in both rocks and hartsalz present in the roof of the carnallite rock, seems to support this hypothesis [29].

Petrographic studies of carnallite rock and hartsalz from the Stassfurt bed uncovered numerous carnallite relicts in hartsalz sylvine. A secondary origin of the hartsalz is confirmed also by rubidium and bromine distribution [42]. The preservation of rock salt interlayers, which in hartsalz become red rather than gray, is consistent with this. The sharp variability of hartsalz over short distances supports its secondary origin. The finds of kieserite and sylvinite relicts in langbeinite and kieserite relicts in polyhalite are evidence of the minerals from which they were formed [16].

Local depletion zones in the Stassfurt bed are up to 20-50 m thick; complete depletion areas in South Harz are up to 10-12 km² [47].

In the interior of the central Polish depression, the Stassfurt bed also mainly consists of carnallite rocks; it is up to 25 m thick. However, on the Klodawa salt structure it consists of kieserite-containing rocks of a smaller thickness (6-8 m). In the Ronnenberg bed of Leine series (GDR), consisting of carnallite at the bottom and sylvinite at the top, deple-

tion zones are associated with anhydrite klippen of the underlying main anhydrite bed. Complete depletion zones of the Ronnenberg bed are confined to large klippen that rise above the potash layer roof and range from 50 to 120 m in diameter. The zones, with an asymmetric oval shape, measure up to 300 m across together with the klippe [43]. Near the depletion zones some of the carnallite rock is sylvinitized. The linear rock salt under the potash bed is often red.

Three potash horizons (bottom to top) are distinguished in the Devonian potassium prairie formation (Saskatchewan, Canada) [32, 33]: Esterhazy (K-1), Belle Plain (K-2), and Paton's Lake (K-3). They consist of carnallite rock and sylvinites; the carnallite rock in the K-1 horizon is found mainly at the bottom; in K-2 mostly at the top. Carnallite rocks are more frequent in some locations, sylvinites in others. The top K-3 horizon consists mainly of sylvinites; carnallite rocks occur only locally, mostly at the bottom and, much less often, throughout the layer. The occurrence areas of overlying potash horizons are increased. Where they consist of carnallite rocks they are thicker than in sylvinite locations [51].

Several depletion zones have been discovered in the Saskatchewan deposit potash horizons [38, 51]. Mostly, they are lens- or mushroom-shaped and consist of pure coarse-grained rock salt. On margins the rock salt is clayey and coarse-grained, with small red sylvine crystal inclusions. The contacts of these zones with sylvinite are uneven and ragged. Carbonate clay interlayers have been preserved in the rock salt; they are also found in sylvinites [41]. Bromine content in halite and sylvine of the depletion zones is higher than in the deposits that enclose a sylvinite layer.

Between Watrough and Kandagar (Saskatchewan) transitions of red carnallite rock to red sylvinite and of both these rocks to rock salt are observed [51]. Halite grains and rare sylvine grains are usually light in the carnallite rock, whereas in sylvinite only halite grains are light, while sylvine grains are red. The red sylvine has an abnormally high rubidium content, also indicating that it was formed from carnallite. Postsedimentary alteration of these rocks is also evidenced by argon content in sylvinites, indicating that they are not of a Middle Devonian age but are Mississippian (339 million years) or even Tertiary (56 million years); the majority of determinations fall on the time between the Mississippian and the Triassic (207 million years).

Both lateral and vertical transitions of massive red carnallite rock to red sylvinite and then to halite rocks are sharp in Saskatchewan potash strata. Sylvinite inherits crystal orientation, iron oxide pigmentation (hematite and fibrous goethite) and rubidium from carnallite. Iron oxides in halite crystals are inherited from sylvine according to their crystallographic orientation. Carnallite substitution was associated with loss of $MgCl_2$ and a corresponding decrease of the thickness of potash layers. A presence of carnallite with the same bromine and rubidium contents as in the carnallite rock has been discovered in the underlying rock salt. This is evidence of descending dissolution processes.

The Salado Permian potash formation (Western Texas and New Mexico, US), widespread in the Delaware and Midland depressions and also overlying the El Capitan barrier reef, consists of rock salt at the bottom; in some of the locations the rock salt includes polyhalite-containing anhydrite beds [25]. The overlying potash zone includes up to 11 potash salt horizons [36]. They occur in the northwestern salt-bearing basin (the Carlsbad deposit). Sylvine, carnallite, kainite, and langbeinite are the most common potash minerals. Kieserite, polyhalite, leonite, glauberite, and thenardite are also found locally.

Sylvinites are predominant in the northern part of the Carlsbad deposit; locally, there is carnallite rock (mainly in the extreme north). In the southern part of the deposit, langbeinite with sylvine and kieserite (sometimes with kainite) are present. Sharp variations of the mineral composition and thickness are typical for potash salt horizons. Often, commercial-grade ores are not found in the entire potash layer, but in isolated peculiarly connected strips (Fig. 3), forming a labyrinth complex [37]. Potash horizons in the southern part of the deposit are usually thicker than in the north.

Four potash horizons are distinguished in a potash mine in the Delaware depression (southeastern New Mexico) (occurrence depth in feet): 700, 800, 850, and 900 [28]. The two middle horizons consist mainly of sylvine and langbeinite; the other two display mostly sylvinite, which is combined with carnallite in the top layer. Sylvinite of the lower layer and langbeinite rock of 800-foot horizon are mined. The lower third of the potash 800-foot hori-

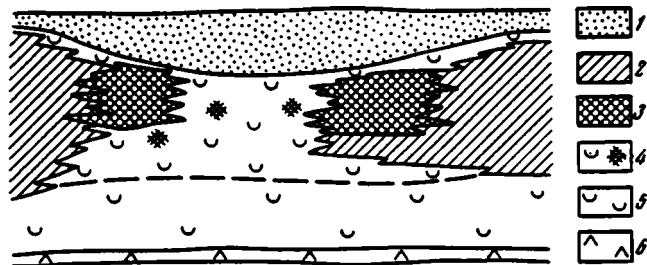


Fig. 5. Replacement and depletion in the potash salt deposit of the Maha-Sarakhan formation, Thailand and Laos [31]: 1) terrigenous rocks; 2) carnallite rock; 3) sylvinite; 4) lixiviation salt; 5) lower rock salt; 6) anhydrite.

zon consists mainly of a langbeinite rock. The lower two-thirds of the overlying part usually consist of a langbeinite rock; in some areas in the northwestern half of the mine field there is also sylvinite. The top is formed of sylvinite. The higher the content of langbeinite rock in a section, the greater its thickness [28].

Depletion zones in the Carlsbad deposit have been found (Fig. 4) in the lower 3-4 m thick sylvinite layer [39]. It consists of three sylvinite sublayers (each 75-90 cm thick), separated by marker interlayers (10-30 cm) of orange rock salt. Sylvine in the sylvinite layers is milk white or red; halite is colorless. In plan, the depletion zones appear as strips or irregular concentric bands, 0.3-106 m wide and 4.5-160 m long. The depletion areas are largest (up to 0.016 km²) in the lower sylvinite layer; in higher horizons they are smaller.

Sylvinite and rock salt contacts in depletion zones are distinct. Kainite, langbeinite, and leonite lenses are found near the contacts. At a distance from the contact, rock salt contains small lenses of recrystallized coarse-crystalline halite and sylvine aggregates and sylvine relicts. Near the contacts, the depletion zones often exhibit small anticlinal folds up to 1 m wide and 15-60 cm in height. The clay interlayers in depletion zones are light or dark brown; in sylvinite they are usually gray. The rock salt of these zones sometimes contains relicts of a sylvinite layer. Where the depletion is incomplete, the thickness of sylvinite layers decreases over a short distance abruptly from 75 to 20 cm.

In the 800-foot potash horizon north of Carlsbad, sylvinite and langbeinite rocks also contain lens-shaped halite bodies, which are depletion zones. They are formed of recrystallized halite free of clay matter. According to Dunbar [28], the differentiation of potash-magnesium minerals in potash horizons is of a primary sedimentary or early diagenetic type; halite bodies in the depletion zones are interpreted as later formations.

Linn and Adams [39] cite the following facts as evidence of selective sylvinite lixiviation in the Carlsbad deposit: 1) consistence of intraformational marking interlayers of orange rock salt and halopelites; 2) sharp contacts of sylvinite layers and the rock salt replacing them; 3) upward decrease of depletion zone areas of sylvinite layers; 4) presence of sulfate potash minerals in depletion zones; 5) lenses of giant-grained halite and sylvine; 6) remains of sylvine layers in depletion zones; 7) small folds near zone contacts; and 8) the brown pigmentation of halopelites in these zones.

Cretaceous (Aptian) potash formations in Brazil and West Africa (Gabon and the Congo) formed in subbasins of an originally unified rift system exhibit similar sections. They vary in thickness from 500 to 900 m. Numerous potash-magnesium salt beds in these formations consist mainly of a carnallite rock and partly of sylvinite. Tachhydrite or bischofite beds are typical for the tops of these formations. Sylvinites usually are found in two lower potash beds or in one or two top beds.

The size and habitus of carnallite crystals suggest that they were deposited from variously concentrated brines. Carnallite has a high but quite variable bromine content and a low rubidium content. Sylvinites in the two regions are assumed to have been formed from carnallite rock. They have a normal bromine content and a low rubidium content.

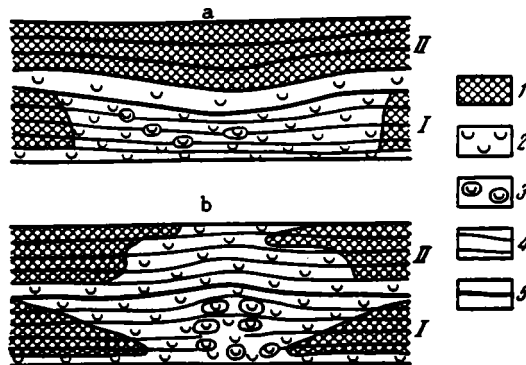


Fig. 6. Depletion zones of sylvinites of first (a) and second (b) types of second potash horizon, Starobinsk deposit [11]: 1) sylvinite; 2) rock salt; 3) areas of coarse crystalline water-transparent halite; 4) halopelite interlayers; 5) basal halopelitic interlayer; I-II) sylvinite layers (I - lower, II - upper).

In the Brazilian Sergipe subbasin, zones of carnallite replacement by sylvinite and subsequent depletion down to halite rock in the two lower potash beds are found over narrow horsts and elevated steps of faults in the subsalt basement. Sylvinitization of the upper carnallite layer is associated with hypergenetic processes [50].

Sylvinites in the Congo subbasin (West Africa) are similar to cis-Uralian variegated sylvinites. Since replacement zones of different potash beds do not match here, their correlations with subsalt disjunctive tectonics have not yet been determined. In the Holle deposit a sylvinite zone in the top potash layers has the outline of an arcuate strip. The lack of reliable predictive criteria of these zones in the first decade was a major obstacle to commercial operation of this mine [44].

The proportion of carnallite rocks in Congo subbasins is 25-35%; in Gabon and Sergipe 15%. The numbers for sylvinite are 2, 5, and 6%, respectively. These data offer a gauge of the substitution process.

A potash salt deposit up to 40 m thick (locally, up to 95 m) in the Cretaceous potash formation at Maha-Sarakhan (Laos and Thailand) consists mainly of carnallite rocks. It also contains sylvine, tachhydrite, and boracite. At the north of the salt-bearing basin (mainly Laos) it is spread over an area of 21,000 km²; in the southern part (Thailand) it covers an area of 36,000 km². Locally, including locations north of Vientiane (Laos), the deposit consists of a high-grade sylvinite, up to 19 m thick, even 34 m in one bore hole. Sylvinite areas of the potash deposit and halite "barrens" are replacement and depletion zones of carnallite rock [31]. Even according to drilling data one observes here the same pattern of carnallite replacement by sylvinites followed by transition to rock salt [35] that is discovered in other potash formations of the world belonging to the chloride subtype (Fig. 5).

One of the youngest (Quaternary) potash formations of the world, discovered in western Danakil depression (Ethiopia), is up to 960 m thick. Its potash horizon in the Masli deposit exhibits this section: bottom - layered fine-grained kainite rock (4-14 m); middle - mixed carnallite-containing rock (3-24 m); and top - sylvinite (0-11 m) with carnallite, kieserite, kainite, and polyhalite insets. The potash horizon is overlain with an erosion by a marker rock salt bed (4.5-15 m). Outcrops of basic intrusions and unique hot chloride brines are found at the center of the depression; salt crusts with carnallite are observed on the day surface. South of Dalol, an additional bed has been discovered by drilling beneath the first potash horizon.

The top potash horizon, called Nostock, is variegated. The middle carnallite-containing member is particularly diversified and includes sylvine, kieserite, and kainite (sometimes up to 10% of each); in addition, there are minor amounts of polyhalite, bischofite, and rinneite. At the bottom of the section there is more kainite; at the top, more sylvine. The middle and top members contain up to 15% anhydrite. The sylvinite is stratified, with peculiarly crumpled anhydrite interlayers. The top sylvinite member has been interpreted by investigators as a second body formed by carnallite-containing rock acted upon by meteoric water in a subsurface setting [34].

The sylvinite member in the Masli deposit has local zones of complete ore depletion ("barrens" of rock salt or anhydrite). three types of zones are distinguished: 1) sylvinite gives way abruptly to a halite-anhydrite rock; 2) sylvinite is superseded laterally

by rock salt (one of the zones is up to 23 m wide); 3) and depletion zones are associated with faults and stretch along them (with giant-crystalline halite). Rock salt of the barrens is similar to sylvinite in appearance; it has the same seasonal stratification, although transitions of sylvinite to rock salt are sharply defined. Sylvinite depletion zones, at least those associated with faults, are of a later origin [8]. Carnallite was substituted by sylvinite, which was then depleted to rock salt according to the same scheme.

Various substitution and depletion zones have been described in potash salt deposits all over the world. The leading theme, everywhere was replacement of carnallite rock by sylvinite and its depletion to rock salt. Sulfate potash-magnesium minerals (hartsalz rocks) were formed in some deposits as a result of replacement by carnallite and especially kieserite-carnallite and carnallite-bearing rocks of a more variegated mineral composition - as well as sylvinite. The former change was characteristic for chloride potash formations; the latter was typical for the sulfate-chloride subtype.

Depletion and substitution zones in potash salt deposits in the USSR were discovered after the Second World War, first in the Verkhnekamsk deposit (1948) and then in Kalus (1953) and Starobinsk (1960). Postwar drilling data suggest similar barrens in potash regions not yet mined (Nepsk, Caspian, Central Asian, and others).

Substitution and depletion zones of potash salt beds forming the lower sylvinite and upper sylvinite-carnallite horizons have been studied for a longer time and in greater detail at the Verkhnekamsk deposit. Although these beds belong to the potash formation of the simple chloride subtype, preserve a gentle occurrence, and are less folded, it was difficult to identify substitution zones in them and describe their location and formation patterns.

The sylvinite horizon of the Verkhnekamsk deposit consists of three red sylvinite beds (Kr-III, Kr-II, and Kr-I), 0.8-5.3 m thick, sometimes swelling up to 10 m, and the upper striated sylvinite bed (A), with an average thickness of 1.8 m. The sylvinite horizon is 7-40 m thick (an average of 20-25 m).

Up to nine potash salt beds have been identified in the sylvinite-carnallite horizon section (indexed by letters from B to K). They consist of a carnallite rock (0.5-28 m in swollen portions) and variegated sylvinite (an average thickness of 0.8-3.4 m).

Transitions of the carnallite rock to variegated sylvinite and of sylvinites to rock salt in this deposit were discovered before the war. At that time, they were regarded as facies phenomena [7] or dynamometamorphic formations [17]. Later, they were classified as sedimentary [2, 5, 18]. Khod'kov [23] was the first to break with tradition and link the development of substitution and depletion zones to sedimentary chlorine-sodium brines extruded upward by lithification of subjacent rock salt; he supported this theory by noting the inherited properties of areas in sylvinitic and overlying carnallitic layers. Nevertheless, later investigators continued to interpret these formations as early diagenetic [9] or primary sedimentary [21]. These authors made valuable contributions to describing the geometry and patterns of these formations in the Verkhnekamsk deposit.

Two types of depletion zone are now identified in this deposit [21]. The first type consists of large rock salt bodies (up to 2.5 km² area in lower sylvinite beds); the second type is represented by local bodies. Large zones are isometric or ellipsoid in plan and conical in section. The depletion zones vary in size from 30 × 50 m to 1 × 2 km and more.

Depletion of sylvinite beds can be complete or partial. In large zones (over 1 km²) it is observed for tens of meters (up to 100 m in Kr-II); in smaller zones, for 10-20 m. Sylvinite interlayers wedge out, and the bed thickness is reduced by about 1/3. Some sylvinite interlayers wedge out for 3-5 m; isolated interlayers wedge out abruptly after 0.2-0.4 m. Where sylvinite in such interlayers gives way to granulated halite, the bed thickness remains unchanged. Depletion zones are often composed of inequigranular rock salt; in the margins it contains milk-white sylvine crystals (up to 2-5 cm). In the depletion zone halite amounts to 91-95%; sylvine drops to 0.2-0.6%, and insoluble residue increases slightly to 1.5-4.9%. The respective figures for sylvinite beds are at most 60-80, 12-37, and 0.8-3.3%.

The following rock succession zonality is observed in carnallite beds B and C of the sylvinite-carnallite horizon: carnallite rock → variegated sylvinite → rock salt in depletion zone. Transitions from variegated sylvinite to rock salt are blurred; distinct stratification is preserved in the rock salt.

At the bottom part of a bed near the contact with the halitic depletion zone, massive sylvinites are common with inclusions of blue rock; at the top, brown distinctly stratified (local) varieties are observed. In some of the depletion zones, sylvinites are succeeded by halite rock through a pseudosylvinites, where sylvinites layers are replaced by red halite interlayers. The bromine-chlorine ratio in red halite is lower than in feathery and granular varieties. In depletion zones of the first type, beds occur relatively calmly with a slight elevation at the center of the zone. Some of the depletion zones are bounded by narrow postsedimentary folds, up to 100 m wide with amplitudes up to 20 m.

Local solid rock bodies of the depletion zones of the second type were formed by folding. Deformed sylvinites interlayers lost their stratification, with the rock becoming spotty. Sylvinites crystals are red, milk-white, and colorless. Depletion zones of the second type are also controlled by folds. Open cracks or cavities sometimes found in them are consistent with the stratification. Local depletion zones are 0.5-20 m long and up to 0.4-5 m high.

The mineral composition of impurities in depletion zone rocks indicates that they were formed or altered in an environment with a lower mineral concentration. Insoluble residues are more coarse-grained than in potash salts. Less MgO and FeO but more Fe₂O₃ are contained in hydromicas.

Depletion zones cover the largest areas in potash beds of the sylvinites horizon. They tend to be associated with sylvinites with a lower KCl and Br content. From the bottom of the section to beds B and C of the sylvinites-carnallite horizon, sylvinites depletion and carnallite rock substitution areas tend to grow smaller. At the top, replacement reappears only in the uppermost potash horizon, I, where it is of a different (hypergenetic) origin.

Studies of replacement and depletion zones of potash salts in the Verkhnekamsk deposit over a long period of time [2, 5, 9, 18, 21] provided details shedding light on their lithology. Even so, their formation and distribution patterns have not been fully clarified. It appears likely that they were formed under the effect of less concentrated chlorine-sodium brines acting upon potash salts; the brines gained access to potash deposits either during early diagenesis, when the brine of the basin was diluted on elevated and peripheral portions of the basin floor, or during subsequent lithification of subsalt rocks, when the brine rose to them through weakened tectonic zones. The former hypothesis provides a slightly better explanation for the development of large substitution and depletion zones of the first type; the second hypothesis fits better the local zones of the second type. It is true that basin floor elevations and weakened zones in subsalt and salt rocks may be of a common tectonic primary origin, suggesting that the explanation should be found in tectonic features of the subsalt beds. However, this theory makes it difficult to predict substitution and depletion zones in this region.

Considerable attention has been devoted to depletion zones in sylvinites beds of the Starobinsk deposit, discovered in 1960 by Fomina. They were investigated by Khod'kov, Ivanov, Fenchai, Yarzhemskii, Protopopov, and others, particularly extensively by Kislik.

Two depletion zones types were distinguished by Kislik [10] in sylvinites of potash horizon 2 of the First Soligorsk Mining Enterprises (Fig. 6). It consists of two sylvinites layers (80-110 cm) separated by rock salt (30-55 cm).

Most depletion zones of the first type are elliptic and stretch sublatitudinally. They range in length from 10 to 50 m (one is 70 m long). Many occur as strings, one after another, also with a sublatitudinal orientation. Sylvinites of the lower layer of the second horizon are usually depleted in zones of this type. The layer thickness is reduced by the total thickness of sylvinites interlayers that disappear from the section. Depletion sometimes also affects the top sylvinites layer; the horizon thickness then is reduced even more. The top of the potash horizon section within these zones has a gentle sag, in many cases forming a low-angle synclinal fold. The sagging produced cracks, which were filled with fibrous halite, sometimes red sylvinites and coarse-grained halite. Dissolution of sylvinites grains and their partial replacement by small yellow halite grains is observed in depletion zones. Bromine content in coarse-grained halite in such zones usually fluctuates widely and sometimes is very low. Typically, its amount in granular halite is the same as in the halite of the sylvinites bed.

Depletion zones of the second type are larger (100-400 m long with an area of up to 0.12 km²). They are round or elliptic and are associated with sublatitudinal and submeridional tectonic faults. Both layers of the sylvinites horizon are depleted, but in the lower layer

this occurs on a larger area (Fig. 6). In the lower sylvinite area (Fig. 6), the overlying sylvinite interlayers are depleted on a larger area than the lower ones; in the unsubstituted part of the layer a "bowl" is formed [10]. Toward the depletion zones, sylvinite interlayers are succeeded by rock salt, usually with a sharp contact. In the near-contact part of these zones, skeletal-zonal sylvine grains are still preserved over a span of 5-10 cm. After that, the halite content rises sharply. Further, in the essentially halitic rock, inclusions of brownish-red and colorless sylvine are sometimes found. Sylvinitic interlayers may be succeeded by similar thin layers of red halite; relict sylvine grains are common.

In the transition zone, halite is distributed at random amid sylvine grains, sometimes replacing them. Halite grains are idiomorphic or rounded; they may be found in strings across layering. At a distance from the contact the layering of depleted rocks becomes unclear because of rock salt recrystallization and fracturing of halopelitic interlayers. At the center of the depletion zones, "swelling mounds" [11] are often formed, up to 10 m long and up to 50 cm high. Rock salt in them is represented by a massive kernel of water-transparent halite, forming a gentle anticlinal fold. The layers in the fold are inconsistent. The basal halopelitic interlayer of the potash horizon at the center of the depletion zone is disrupted; the cracks are filled with crosscutting halite veinlets.

Nestlike accumulations of epigenetic halite and sylvine crystals (1-15 cm) are associated with tectonic faults. Xenomorphic milk-white or pink sylvine grains have a red fringe. Halite crystals are often water-transparent, sometimes opaline, with blue or pale purple shades. The nests contain halopelitic breccia, carbonates, and anhydrite. Pyrite is normally found in the insoluble residue.

Depletion zones of both types are usually associated with weakened tectonic zones, indicated by faults in the subsalt deposits and cracks in halogenous rocks. Depletion zones in the second potash horizon have been estimated to account for 15-20% of its area [10].

Depletion zones have also been found in the second potash horizon of the Second Soligorsk Potash Enterprise and the third potash horizon of the First Soligorsk Enterprise. They are also confined to tectonic faults, and exhibit similar morphology and a typical submeridional orientation. Lixiviation traces are observed in some of the locations.

The submeridional and sublatitudinal orientations of depletion zones in the potash horizons of Starobinsk deposit suggest that they were formed by the action of chlorine-sodium brines extruded during lithification of salt-bearing deposits [10, 24], rather than by primary sedimentary processes postulated by Yarzhemskii. Depletion zones of the first type were formed during early diagenesis; those of the second type are late diagenetic (catagenetic). Petrographic investigations by Petrov and Protopopov [20] discovered that lixiviation brines also contributed to development of depletion zones in the potash horizon near western and central tectonic faults. This is confirmed by a loss of bromine, fibrous halite veinlets, a high concentration of carbonates in insoluble residues, and the presence of authigenic quartz crystals and fine-prismatic anhydrite in the residue.

In the western margin of Starobinsk deposit, potash horizons are first depleted at the section top, giving way to a clay-carbonate member with red halite interlayers ("pseudo-sylvinitic"); they are then succeeded by a halopelitic member with hematitic interlayers. Chlorine salts gradually disappear from the rocks of the horizon and CaSO_4 content is increased. Halopelites contain the same impurity and hematite interlayers the same quantities of Fe_2O_3 as insoluble sylvinite residues. The present occurrence of hematite interlayers in the above-salt strata suggest that the Upper Famennian potash-bearing formation in the past extended beyond its current outline. It was destroyed by ancient lixiviation (near the "lixiviation edge"). The duration and multistadiality of the processes are indicated by sagging troughs with increased Upper Cretaceous, Paleogene, and Neogene thicknesses.

In the Ciscarpathian trough, with a high clay content of potash-bearing deposits, they are represented mainly by sulfate potash-magnesium salts and often occur directly under hydrated Quaternary rocks; hypergenetic alteration is significant. There is schoenite and polyhalite (near the salt mirror); higher up the section there are (or as veinlets in salt rocks) glaserite, syngenite, astrachanite, epsomite, and especially mirabilite are found. The latter mineral also sometimes forms placers at the top of langbeinite-kainite rock beds [13].

Different sylvinite barrens are also known in the Ciscarpathian region. Two types of such zones have been studied in [12] in the field of Northern Kalus.

Barrens of the first type are associated with juncture areas of the sides and the axial portion of a transverse synclinal fold, where layers are bent sharply in the sylvinite bed with the appearance of disharmonic folding and small disjunctive faults. Locally, sylvinite layers are split and partly replaced by red halite. Later, they are succeeded by brecciated salt-bearing clayey rock. In this rock the cracks are filled with fibrous, sometimes red, halite ("pseudosylvinitic"). Such a linear barren divides sylvinitic beds of the northern field and its Zagrobske section [12].

Barrens of the second type have been discovered in the axial part of the transverse fold to the rise of the sylvinite bed. In larger zones, sylvinite interlayers are also replaced by red halite layers with a transition to fractured salt-bearing clayey rocks. The cracks are filled with fibrous or red halite. In smaller barrens, to the strike, sylvinite gives way to fine-stratified clay rock salt. The sylvinite placer bottom is partly brecciated and partly consists of red halite. Its thickness is reduced. A member of finely stratified halite rocks sometimes is superimposed on the cut upper part of the sylvinite placer.

Barrens of the second type seem to be associated with early diagenetic alteration of the placer in the northeastern margin of the halogenic basin; barrens of the first type are of a later origin, associated with subsequent tectonics.

In the Nepsk deposit (East Siberia), carnallite rock gives way to sylvinites in potash horizons. Horizons 3-5 of sylvinites include elongate halitic zones. Investigators have interpreted these transitions by facies, while others have attributed them to substitution of sylvinites for carnallite rocks and depletion to rock salt accompanied by formation of sagging valleys [6].

The Kungur potash-bearing formation of the Caspian syncline belongs to the sulfate-chlorite subtype according to the mineral composition of the potash-magnesium salts. Its similarity to Zechstein potash formation of Western Europe implies analogies in the lithology of the substitution and depletion zones. In the lower potash horizon of the Kungur formation in the Caspian region, just as in the lower (Stassfurt) bed of Zechstein in the GDR, these transitions are observed: from kieserite-bearing carnallite rock to kainite-bearing sylvinite, to kainite-langbeinite sylvinite and polyhalite-bearing sylvinite with glaserite eyelets and veinlets, to rock salt with poor potash mineralization [22]. The alteration of potash salts in the Caspian salt domes is distinct in the axial parts of folds and in fault zones, where zonality and parageneses are sometimes disrupted and complicated. Some of the zones disappear or are seen as wedges, and potash-magnesium salt veinlets appear.

Sylvinites of substitution zones in the Caspian region are usually variegated and brecciated with kainite, langbeinite, polyhalite, and glaserite nests. Lixiviation is also observed in fractured zones; the breccia contain mostly anhydrite, halite, and gorceyite neomorphs. There are also later formations of giant-crystalline halite and sylvine, mostly red.

Bromine loss was slight at sylvinite-for-carnallite substitution. Bromine-chlorine ratios in the kainite-containing sylvinite are almost the same as in the carnallite rock. For kainite-langbeinite sylvinites these ratios are in the field of normal sylvinites. It is only in polyhalite-bearing sylvinites that the values are near the lower boundary of the sylvinite field and outside it [22]. Rocks salt of the depletion zone contains loeweite, locally leonite, with anhydrite polyhalitization.

Halite-carnallite rock in the overlying bed of Kungur potash salts in the Caspian region is replaced by sylvinites, which exhibit successively kainite and polyhalite. Sylvinites are brecciated; on areas of intensive fracturing, salt removal and loss of bromine content are observed, while polyhalite, glaserite, and syngenite amounts are increased [22].

In the Permian potash formation of the Dnieper-Donets depression, kieserite, kainite, and langbeinite have been discovered in the carnallite rock horizon in some areas (drilling data); it is indirect evidence of substitution zones in potash salt beds.

Finally, the Upper Jurassic of potash formation in Central Asia (Karlyuk and Gaurdak deposits) potash horizons consist of both carnallite and sylvinite rocks. From north to south at Gaurdak, there is a traceable tendency for succession of carnallite rock by carnallite-sylvinites followed by sylvinites, and in the extreme south by rock salt [3]. Sylvinites also supersede carnallite-containing rocks in southeastern Karlyuk and Okuzbulak. The sylvinitic portion of the middle horizon includes a blue sylvinite bed at Karlyuk deposit.

A regular succession of carnallite-containing rocks by sylvinites and in the extreme south also by rock salt in the region of Central Asia has been interpreted by some investigators as a facies-sedimentary phenomenon. However, a noticeable recrystallization and traces of partial dissolution of sylvinite and rock salt, sylvinite substitution by halite and carbonates, and later neomorphic sylvine crystal xenomorphs have also been described in this region. In addition, carnallite grains are sometimes replaced by sylvine and halite, preserving the original configuration. Like carnallite grains, sylvine grains are pigmented by pelitomorph hematite, sometimes with concentrically zonal distribution of microinclusions. With decreasing carnallite content, the bed thickness is also decreased. This suggests carnallite substitution by sylvinite and sylvinite depletion to rock salt. An additional sign is the fact that rich sylvinites are the principal rubidium carrier in this region; usually, it is contained in carnallite rocks [19]. Intensive disjunctive tectonics and the block structure of the potash-bearing Gaurdak-Kugitang area are favorable factors.

Zones of potash salt deposit substitution and depletion can be found, in principle, in any potash formation. Rocks of these zones usually bear traces of the effect of less concentrated brines. The nature of these brines and the time of the substitution and depletion processes cannot always be determined unequivocally. Certain facts suggest that the placers were altered during early diagenesis (before sediment lithification) and during the post-diagenetic period (by rising brines). The tectonic activity determines the location of substitution and depletion zones either directly or indirectly. Each potash formation subtype is characterized by a specific alteration sequence of the mineral composition of rocks of the zones described above. In the hypergenesis zone, selective lixiviation produces not only only residual gypsum-clay "caps," but also peculiar zones of potash salt substitution.

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BEHAVIOR OF SCANDIUM IN BED-INFILTRATION ORE-FORMING PROCESSES

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Scandium (and possibly some elements of the lanthanoid group) forms epigenetic ore accumulations during the bed-infiltration process; it is extracted from surrounding pyrite-bearing rocks on the advancing front of intrastratal oxidation. At some distance from the front it is redeposited on a neutralization (alkaline) geochemical barrier. Instability constants of $\text{Sc}(\text{OH})_4^-$ and $\text{Sc}(\text{CO}_3)_2^-$ complexes are estimated experimentally, and the physical and chemical conditions of Sc behavior in exogenous natural settings are characterized.

As more information is accumulated and analytical methods are improved, exogenous bed-infiltration deposits (associated with interstratal oxidation zones) are increasingly seen as highly complex entities. Besides uranium, ores of these deposits often contain significant amounts of selenium, rhenium, molybdenum, and vanadium [2, 3, 7, 13-15, 17, etc.]; molybdenum and vanadium metallization is sometimes superior in magnitude to uranium concentration. The present paper describes a valuable component - scandium - which sometimes forms epigenetic accumulations in uranium ore roll zones and is found in technological solutions during uranium extraction by underground lixiviation (UL) according to sulfuric acid and bicarbonate chemical processes (in amounts of fractions of a milligram per liter).

Scandium in ore and ore-containing rocks has been measured by instrumental neutron activation methods [6, 10] with a sensitivity of 0.1-0.3 g/ton in silicate rocks.

In the infiltrational uranium deposits in deltaic Lower Senonian (Upper Cretaceous), for which scandium contents are known best, ore-containing rocks consist of gray loose medium- and small-grained feldspathic-quartzose sands with detrital chlorite, biotite, and muscovite grains, thin lenslike interlayers, and clay rolls. The zone of unoxidized rocks contains segregates of diagenetic and epigenetic pyrite, 0.5-2.5%, rare glauconite grains, and coaly and phosphate bone remains. The heavy fraction includes ilmenite, rutile, and zircon. The sand is of a low carbonate content: CO_2 content varies in the range of 0.1-2.0%. Red-pink and brownish-yellow iron hydroxides are abundant in the intrastratal oxidation zone.

Uranium metallization is associated with selenium, rhenium, and vanadium concentrations, creating a system of embedded ore rolls (Fig. 1).

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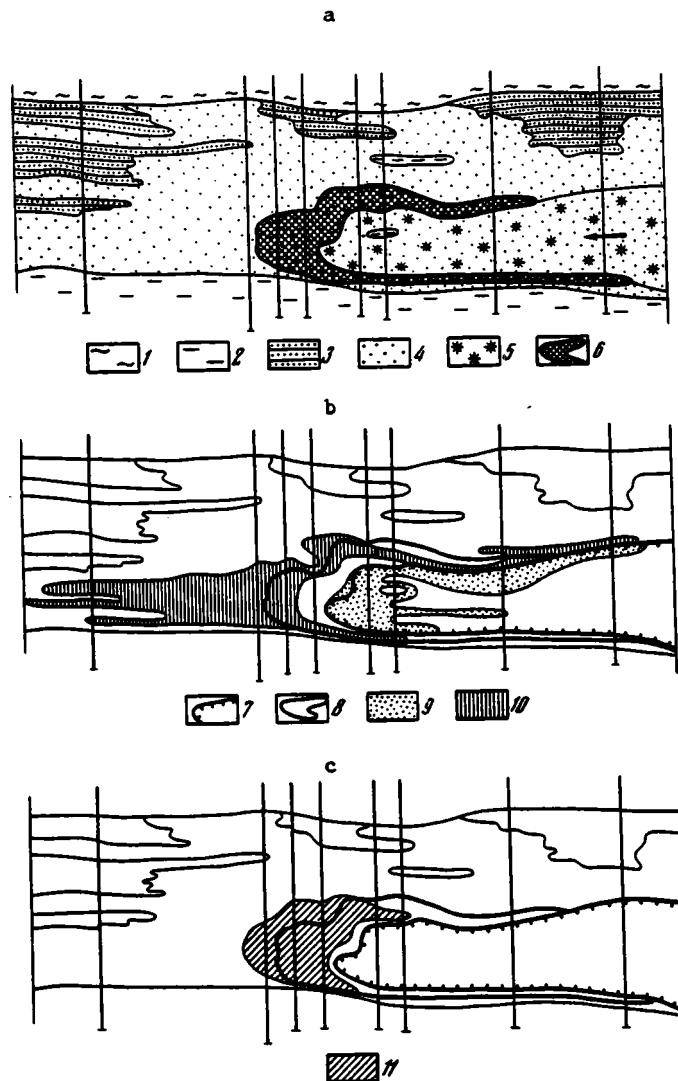


Fig. 1. Positions of uranium (a), selenium and rhenium (b), and scandium (c) ores in the profile of stratal epigenetic zonation in a deposit in deltaic Lower Senonian sediments: 1) clay; 2) siltstone; 3) carbonate sandstone; 4) sand; 5) stratal oxidation zone; 6) uranium metallization; 7) boundary of stratal oxidation zone; 8) uranium metallization contour; 9-11) metallization (9 - selenium, 10 - rhenium, 11 - scandium). The arrow indicates the direction of formation water flows.

Scandium concentrations in unaltered gray rocks amount to 2-5 g/ton; scandium concentration increases progressively with increasing proportion of silt-clay particles.

Scandium distribution in the profile of stratal oxidative ore-controlling epigenetic zonation is characterized by Table 1.

According to the data in Table 1 and Fig. 1, scandium accumulations form an epigenetic zone in this deposit. The zone is inscribed into the "bag" of a uranium-ore roll, slightly shifted toward the rhenium metallization subzone and oxidized ore-free rocks. Sands are enriched in scandium compared with the initial varieties on average by a factor of 1.6; this is associated with depletion of stratal-oxidized rocks by some 30%.

Because of low concentrations in the ore, the mineral form of stratal-infiltrational scandium accumulations remains unclear. Hypothetically, it is the hydroxide $\text{Sc}(\text{OH})_3$. Highest (60-110 g/ton) scandium contents in the ore zone are associated with glauconite grains,

TABLE 1. Scandium Distribution in the Profile of Ore-Controlling Epigenetic Zonality

Epigenetic zone	No. of specimens	Sc content, g/ton (top: maximum value; bottom: mean value)
Stratal oxidation	51	$\frac{1-5}{2,7}$
Metallization:		
Selenium	121	$\frac{1-20}{3,7}$
Uranium	80	$\frac{3-25}{6,2}$
Rhenium	153	$\frac{2-20}{5,7}$
Unoxidized ore-free rocks	37	$\frac{2-7}{3,8}$

hydromicaceous and montmorillonitic clay mineral segregates, and phosphate remains. Scandium is concentrated in the heavy sand fraction,

Scandium oxide is soluble in acids, particularly in concentrated acids with heating [4]; it forms Sc^{3+} and ScOH^{2+} ions. Amorphous or crystalline scandium hydroxide (at a temperature of 160°C) can easily be obtained by neutralizing acid solutions; in the temperature interval of 250-255°C it is converted to Sc_2O_3 . Precipitation of $\text{Sc}(\text{OH})_3$ by ammonia or strong alkalis begins, according to Komissarova [4], at pH 4.8-4.9, attaining the optimum at pH 8.5. A further alkalinity increase results in a noticeable $\text{Sc}(\text{OH})_3$ dissolution, presumably through formation of a scandiate ion [1]. At high concentrations of respective addenda, scandium forms chloride, and sulfate complexes in an acid medium; in a subneutral-moderately alkaline medium it gives rise to carbonate and hydroxycarbonate complexes. Most of these substances have not been investigated sufficiently.

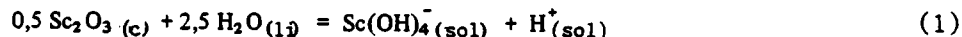
Reference materials [8] cite thermodynamic constants (especially Gibbs standard free energy) only for two solid phases (Sc_2O_3 and $\text{Sc}(\text{OH})_3$), the ion Sc^{3+} , and monohydroxy complex ScOH^{2+} , as well as four fluorine complexes of the ScF^{2+} - ScF_4^- series. With these values one can quantify scandium behavior in a standard acid medium (disregarding the effect of chloride and sulfate ions). For subneutral and relatively alkaline media, including carbonate media corresponding to initial infiltrational ore-forming systems, there is no appropriate analytic information for reliable thermodynamic calculations of scandium contents.

As a way to fill this gap, we studied experimentally the solubility of scandium oxide: a) in a strong alkaline region in absence of carbonate components; and b) in a moderate alkaline carbonate medium. Scandium in solutions was determined with a Polivak E-1000 plasma-tron (with a sensitivity of 0.01 mg/liter). An aliquot (15-20 ml) was evaporated on a water bath; the specimen was carefully neutralized with hydrochloric acid and reevaporated. The residue was dissolved in 0.7 M HCl, placed in a 25-ml measuring retort, brought to a level mark by adding the same acid, and subjected to measurement. Scandium content was estimated from a calibration chart.

The first series of tests investigated Sc_2O_3 solubility in caustic soda solutions at three pH values: 14, 13, and 12.5. The system reached equilibrium on days 20-25. The results of the experiments are given in Table 2 and Fig. 2a.

The measurement points lie on a straight line; its slope is 45° (see Fig. 2a). Thus, increasing pH by a unity improves Sc_2O_3 solubility by an order of magnitude.

This may be the case if scandium in the solution is represented by a tetrahydroxide complex $\text{Sc}(\text{OH})_4^-$, whose equilibrium with the solid phase Sc_2O_3 is described by the reaction



and the corresponding functional relationship

TABLE 2. Results of a Study of Sc_2O_3 Solubility in Alkaline Carbonate-Free Media

Test number	pH	Ionic strength, μ	$-\lg c_{\text{Sc}}$	Activity coefficient of single-charged ions, $-\log \gamma'$	$-\lg a_{\text{Sc}(\text{OH})_4^-}$	$-\lg K_{p1}$
1	14,0	1,0	4,65	0,24	4,89	18,89
2	13,0	0,1	5,66	0,12	5,78	18,87
3	12,5	0,05	6,25	0,09	6,36	18,86

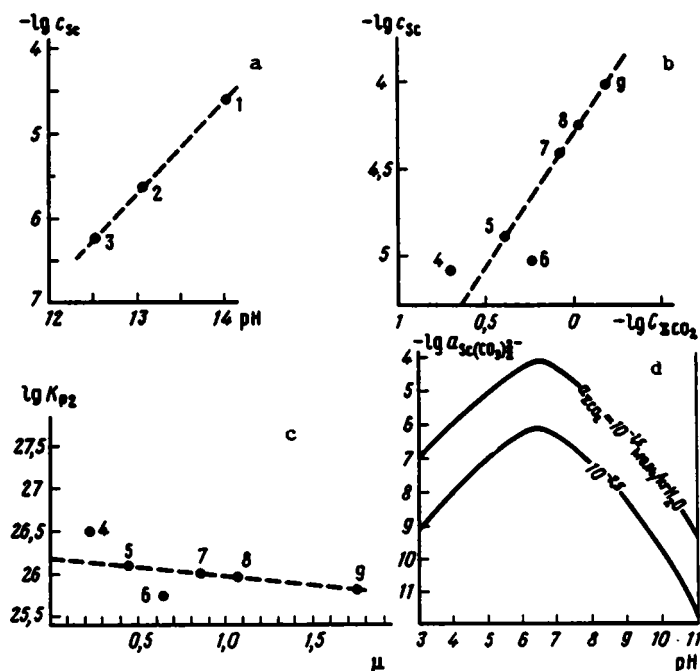


Fig. 2. Results of an experimental study of Sc_2O_3 solubility in standard conditions: a) Sc concentration vs pH in alkaline solutions; b) same vs ΣCO_2 in carbonate solutions (at pH 9.4); c) concentration constants of equilibrium of reaction (2) vs ionic strength of solution μ ; d) calculated relation of activity of $\text{Sc}(\text{CO}_3)_2$ (in equilibrium with Sc_2O_3) as a function of pH at various $a_{\Sigma\text{CO}_2}$. Numbers at curves identify tests (1-3 - first series; 4-9 - second series).

$$K_{p1} = \lg a_{\text{Sc}(\text{OH})_4^-} - \text{pH}, \quad (1a)$$

where K_{p1} is the constant of reaction (1), and a is activity.

With experimental data and the Debye-Hückel equation [8], where $\bar{a}$ for a single-charged ion $\text{Sc}(\text{OH})_4^-$ is set at 3.5, we can estimate the equilibrium constant of reaction (1). Based on three determinations, it is $10^{-18.85}$.

Accordingly, $\Delta G_{298.15}^\circ \text{Sc}(\text{OH})_4^- = -333.56$ kcal/mole, and $K_{\text{inst}} \text{Sc}(\text{OH})_4^- = 10^{-28.9}$ (where K_{inst} is the instability constant of the complex compound).

According to these data, the concentration in an alkaline solution of scandium bonded to $\text{Sc}(\text{OH})_4^-$ in an equilibrium with the solid phase Sc_2O_3 at pH 14 is 10^{-3} g/liter; at pH 13, 10^{-4} g/liter; at pH 12, 10^{-5} g/liter... at pH 9, 10^{-8} g/liter. In the range of alkaline-acid

TABLE 3. Results of a Study of Sc_2O_3 Solubility in $(\text{NH}_4)_2\text{CO}_3$ Solutions at a Stable pH (9.4)

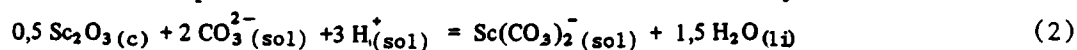
Test number	$c_{\Sigma \text{CO}_3}$, mole/kg H_2O	$-\lg c_{\text{Sc}}$	Ionic strength, μ	$-\lg c_{\text{CO}_3^{2-}}$	$\lg K_{p2}^c$
4	0,2	5,08	0,21	1,68	26,48
5	0,4	4,87	0,42	1,38	26,09
6	0,6	5,04	0,64	1,20	25,68
7	0,8	4,39	0,85	1,08	25,97
8	1,0	4,21	1,06	0,98	25,95
9	1,5	4,03	1,76	0,80	25,77

environments existing in natural groundwater (pH 6.6–8.5), the role of this complex is negligible and can be ignored in estimating scandium migration conditions in the hypergenesis sphere.

In the second series of experiments we studied the effect of ΣCO_2 concentration on scandium solubility (in the range of 0.2–1.5 mole/kg H_2O) at a stable final pH of 9.4. The solvent was an ammonium carbonate solution. The system reached equilibrium in approximately 9 months.

The measurement results are presented in Table 3 and Fig. 2b. The points generally fit on a straight line; a tenfold increase of ΣCO_2 leads to an increase of scandium concentration in the solution by about two orders of magnitude. This means that there are two carbonate molecules per scandium atom in the initial compound. Apparently, it is the bicarbonate complex $\text{Sc}(\text{CO}_3)_2^-$, suggested in earlier studies [4, 16, etc.].

The equilibrium of this compound with scandium oxide is described by the reaction



and the related equation

$$\lg K_{p2}^c = \lg c_{\text{Sc}(\text{CO}_3)_2^-} - 2 \lg c_{\text{CO}_3^{2-}} + 3 \text{pH}, \quad (2a)$$

where K_{p2}^c is the concentration constant of reaction (2), and c is concentration.

Table 3 also gives calculated concentration constants for the equilibrium of reaction (2) for six experiments; Fig. 2c plots these constants versus ionic strength of the solution. We see that, of the six characteristics, four fit on a straight line, like in Fig. 2b. There is deviation at points 4 and 6, situated almost symmetrically relative to the general line. This allows us to adopt average data as admissible estimates of the thermodynamic equilibrium constant of reaction (2). This constant, defined by extrapolating the results of tests 5, 7, 8, and 9 to zero ionic strength, is $10^{26.2}$. Hence, $\Delta G_{p2}^0 - 35.7$ kcal/mole, $\Delta G_{298.15}^0 \text{Sc}(\text{CO}_3)_2^- = -420.5$ kcal/mole, and $K_{\text{inst}} \text{Sc}(\text{CO}_3)_2^- = 10^{-17.8}$.

Figure 2d plots the activity of scandium bonded to $\text{Sc}(\text{CO}_3)_2^-$ in equilibrium with Sc_2O_3 vs pH at two fixed values of $a_{\Sigma \text{CO}_2}$: $10^{-2.5}$ (which are typical for infiltrational hydrogeochemical systems) and $10^{-1.5}$ mole/kg H_2O (which are frequent in industrial solutions in the treatment of infiltrational deposits by underground lixiviation according to the bicarbonate scheme). The scandium oxide solubility peak in a carbonate environment falls in the interval of pH 5.0–7.5 (with a maximum at pH 6.3). Almost neutral and low-acidity media are thus favorable for scandium migration.

Correlation between scandium oxide solubility and pH adjusted for all known and thermodynamically estimated forms of existence of this element in solution (the ion Sc^{3+} , the hydroxide complexes ScOH^{2+} and $\text{Sc}(\text{OH})_4^-$, and the bicarbonate $\text{Sc}(\text{CO}_3)_2^-$) is plotted in Fig. 3.

The chart indicates that Sc oxide is highly soluble in a strongly acid region. At pH 4 it is 10^{-4} g/liter; at pH 3 it is already more than 10 g/liter. In less acid media (at pH 5–7) the solubility of this compound is controlled by the carbonate content of the hydrochemical environment; at $a_{\Sigma \text{CO}_2}$, which is usual for natural infiltrational water systems ($10^{-2.5}$ mole/kg H_2O), it is at a level of 10^{-5} g/liter, which is equal to the sensitivity threshold of the analytic method used. As the solution becomes more alkaline, the scandium concentration equilibrated with Sc_2O_3 declines gradually to 10^{-6} g/liter at pH 8 and to 10^{-7} g/liter at pH 9–10. An improved Sc_2O_3 solubility due to formation of $\text{Sc}(\text{OH})_4^-$ ion is noted only in a heavily alkaline medium starting from pH 10.

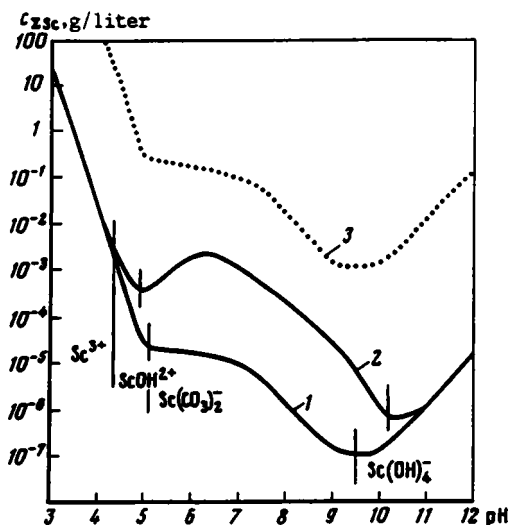


Fig. 3. Calculated Sc concentration vs solution pH (at 25°C disregarding ionic strength): 1-2) in equilibrium with Sc_2O_3 at $\alpha_{\Sigma\text{CO}_2}$ of $10^{-2.5}$ and $10^{-1.5}$ mole/kg H_2O ; 3) in equilibrium with $\text{Sc}(\text{OH})_3$ at $\alpha_{\Sigma\text{CO}_2} = 10^{-2.5}$ mole/kg.

In ordinary formational waters, with close-to-neutral and moderately alkaline media, scandium concentration thus cannot exceed 10^{-6} g/liter, i.e., it is beyond the sensitivity of the existing analytic methods. Presumably, these concentrations are 10^{-7} - 10^{-8} g/liter (in ocean water Sc content is $4 \cdot 10^{-8}$ g/liter [5, 12]). A significant rise in carbonate content of solutions in the pH range of 5-8 raises the solubility curve to fractions of a milligram and several mg per liter. This makes it possible to extract scandium by underground lixiviation not only with an acid scheme but also with a bicarbonate scheme, although the former should be more effective. Scandium yield into solution can be raised largely if its mineral phase is represented by the hydroxide form $\text{Sc}(\text{OH})_3$, whose solubility in all environments is estimated to be higher by four orders of magnitude than that of anhydrous Sc_2O_3 (see Fig. 3).

All these data suggest that, in ordinary infiltrational oxygenated water with an initial moderately alkaline reaction (pH 7-8) and a low concentration of ΣCO_2 (10^{-3} - 10^{-2} mole/kg H_2O) — an environment responsible for epigenetic uranium, selenium, rhenium, molybdenum, and sometimes vanadium metallizations — scandium cannot be transported in tangible amounts because of a low solubility of scandium oxide in such environments. How, then, are exogenous scandium accumulations formed in metalliferous epigenetic zones? An answer could be provided by an analysis of variations of the acidity of hydrogeochemical environments across the profile of ore-controlling zonality.

It has been demonstrated in [13, 14] that, if the epigenetic oxidation zones evolve after rocks rich in sulfidic sulfur (mainly, pyrite) and poor in neutralizers (alkalis and alkaline earths), there is a sharp drop of pH at the advancing front of the epigenetic oxidation zone. Tests with oxidizable carbonic quartzites and phyllites have shown [11] that pH can drop to 4.0-3.0. Scandium then can actively be lixiviated from oxidized rocks, enriching formational water to 10^{-4} g/liter and more. Beyond the wedging-out of stratal oxidation zones in gray rocks, where acidulated water solutions are neutralized by interacting with minerals containing alkalis and alkaline earths (carbonates, hydromicaceous and montmorillonitic clay minerals, micas, and feldspars), dissolved scandium would be hydrolyzed and precipitated as $\text{Sc}(\text{OH})_3$. The process can easily be reproduced in a laboratory.

The region of epigenetic scandium reprecipitation (the region of higher pH of acidulated formational waters) by and large should coincide with uranium ore accumulation zones (zones of contrastive decrease of Eh), although in high-pyrite rocks relatively rich in neutralizers it may tend to be associated with the rear part of the uranium-ore roll. In rocks with a low neutralizer content, they should be at the front of the roll or outside it.

This leads to two important conclusions.

One is that, during the course of the formation-infiltrational process in a pyrite-bearing lithologic environment, scandium, initially contained in a sandy rock, probably in a hard-to-decompose compound, is converted to exogenously redeposited and soluble mineral form (the solubility of $\text{Sc}(\text{OH})_3$ in standard conditions is higher than that of Sc_2O_3 by four orders of

magnitude). This may be the factor responsible for intensive migration of scandium from the ore into the technological solution, during underground lixiviation, even though its concentration in the ore is just above 1 clarke.

The second conclusion is that the effect of a sharp drop of pH in the hydrogeochemical setting, backgrounded by the advance of formation oxidation zones, can likewise transfer into water solution and precipitate during subsequent neutralization a set of other elements of Mendeleev's periodic group III, migrating actively in an acid environment. They include some of the lanthanoids, which in the acid region have solubility curves close to that computed for scandium. Some of these elements have already been established in industrial solutions during underground lixiviation (in concentrations of tenths of a mg/liter and several mg/liter) in this deposit in pyrite-bearing deltaic Lower Senonian sands. Stratal-infiltrational deposits of this kind may become locations for mining a large set of elements, including valuable and scarce metals, by an economical underground lixiviation according to the acid scheme. At high acidity (pH 3.5-1.0) of working solutions, it is possible to extract from ore not only mobile additives of infiltrationally redeposited scandium and its geochemical analogues, but also these metals, present originally in the surrounding sands in a hard-to-decompose form. Separation of these two types of concentrations of mineral components extracted by these processes is a subject for a future study.

From the preceding discussion it should be clear that a search criterion for scandium formational-infiltrational ores (and probably associated rare-earth metals) should be wedging out areas of stratal oxidation zones developed in permeable sandy rocks high in sulfidic sulfur (mainly, pyrite) and relatively poor in neutralizers.

Systematic testing of such locations and infiltrational uranium (and also molybdenum, rhenium, and vanadium) ores in pyrite-bearing rocks of the sedimentary cover for scandium and its geochemical analogues is recommended.

Several conclusions have been drawn from this study.

1. Scandium can be a companion of uranium in stratal-infiltrational metallization processes due to its extraction by formational water from surrounding pyrite-bearing sedimentary rocks on the advancing front of stratal oxidation and precipitation in the adjacent part of the gray unoxidized rock zone. Unlike uranium, selenium, rhenium, and molybdenum supplied by oxygenated formational waters from afar and precipitated on the reductive geochemical barrier, the redistribution of scandium in the profile of stratal epigenetic zonality is local and controlled by a drop of formational water pH in the frontal part of the oxidation zone and subsequent neutralization of these waters downstream (precipitation on neutralizational or alkaline geochemical barriers).

2. Approximate instability constants have been measured experimentally for the tetrahydroxide scandium complex $\text{Sc}(\text{OH})_4^-$ and the bicarbonate complex $\text{Sc}(\text{CO}_3)_2^-$: $10^{-28.9}$ and $10^{-17.8}$. Combined with thermodynamic constants from reference books for the ions Sc^{3+} and ScOH^{2+} , the oxide Sc_2O_3 , and the hydroxide $\text{Sc}(\text{OH})_3$, these data reveal the overall scandium behavior in exogenous settings, indicating that it can migrate actively in an acid medium (in pH < 4 in concentrations over 10 mg/liter) and limited migration in close to neutral carbonate environments ($n \times 10^{-6}$ g/liter and less). A theory has been developed describing the redistribution of this metal during stratal-infiltrational processes and its extraction from the earth's interior during underground lixiviation of exogenous epigenetic deposits.

3. Similarities in the physicochemical behavior of scandium and certain lanthanoid elements in water solutions suggest that these metals can also be accumulated in a mobile form (provided a favorable lithologic and geochemical setting) at the boundary of the zones of stratal oxidation of pyrite-bearing rocks.

4. The search criterion for infiltrational ore accumulations of scandium and its geochemical analogues is wedging out of stratal oxidation zones in rocks with a high content of iron disulfide and relatively low concentrations of neutralizers.

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GÜMBELITE: NEW FINDS IN SHUNGITE-BEARING KARELIAN

ROCKS - DIAGNOSIS AND GENESIS

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UDC 549.1:553.983(470.22)

New manifestations are described of a rare dioctahedral mica of the polytype modification $2M_2$: gümbelite. X-ray powder patterns can be used to diagnose the dioctahedral mica $2M_2$ in the presence of other polytypes. In portions of the section profile a mix of the dioctahedral micas $2M_1$ and $2M_2$ was found in all horizontal veinlets investigated. Regular relationships between these polytypes are established. The main factors controlling gümbelite formation are discussed.

Dioctahedral micas of the polytype modifications $1M$ and $2M_1$ are found in diverse geological environments. Mineralogic observations [9] and experimental data [10] suggest that at temperatures above 300-350°C muscovite $2M_1$ is predominant. At lower temperatures, two modifications ($2M_1 + 1M$) or only $1M$ muscovite are found. The dioctahedral mica $2M_2$ is much less common. In 1966 it was established for the first time that a micaceous asbestoslike mineral, similar to the one described by Gümbel in 1868 [21] and called gümbelite after him, belongs to dioctahedral micas of the polytype modification $2M_2$. Gümbelite diagnosis has a

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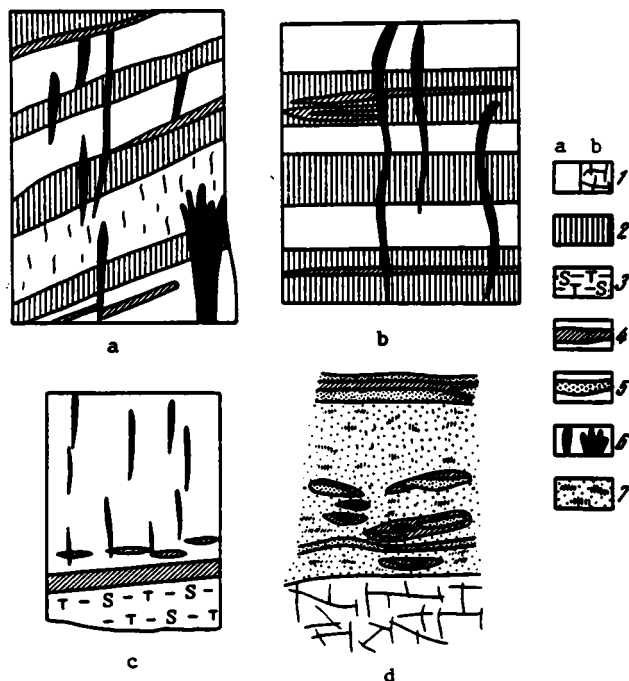


Fig. 1. Position of gümbelite veinlets in section (scale 1:1): a) at contact of shungites II-III; b) in shungites II; c) at contact of shungites II and shungite-containing calcareous tuffites; d) around pyrite lenslets; 1) shungite II (a - massive, b - with cleavage cracks); 2) shungite III; 3) shungite-containing calcareous tuffite; 4) gümbelite veinlets; 5) pyrite lenslets and veinlets; 6) vertical veinlets of various composition; 7) pyritization and gümbelitization zones in shungite-containing rocks.

long history. For a long time it was treated as part of the pyrophyllite group [21]. X-ray investigations for studying it were first used by Aruja [18], who demonstrated the similarities of gümbelite and hydromuscovite structures. Comparing powder patterns of dioctahedral micas of different polytype modifications, Sokolova [14] advanced the hypothesis that gümbelite belongs to $2M_2$ micas. A simultaneous detailed and comprehensive investigation of Karelian gümbelite [5] yielded a specific description of its structure, also placing it with the polytype modification $2M_2$.

In the 100 years since its discovery, gümbelite has been described in several regions: in Carboniferous clay schists of the Franconian Forest [19], graptolitic Carboniferous schists in the eastern part of the Thuringen Forest [21], coal-bearing strata in Donets and Kuznets Basins [2, 4, 17], and carbon-containing Jurassic deposits in Southern Daghestan, Northeastern Azerbaijan, and Central Caucasus [8]. The Karelian gümbelites have been described in the literature extensively [5, 12, 13]. Quartz, pyrite, chlorite, dickite, and kaolinite have been found in paragenesis with gümbelite; its formation conditions correspond to anthracite (A) or semianthracite (SA) metamorphism stages [2].

In [13] the question was raised as to why, despite the general widespread occurrence of shungitic schists in the Onega trough, gümbelite has been located only in a small area near the Shunga Village. Considerable drilling in the past few years in the area of the Onega trough provided new information for detailed analysis of the genesis of shungitic rocks and their mineral features. Primary documentation from the Zazhagin shungite deposit compiled by S. V. Kupryakov, the senior geologist of the Kondologa expedition, reports gümbelite finds; no laboratory determinations of the mineral have been performed. We have formed a collection of micaceous minerals as part of a study of the mineral composition of shungite-bearing rocks from the Zazhagin deposit. The study pursued three objectives: 1) gümbelite

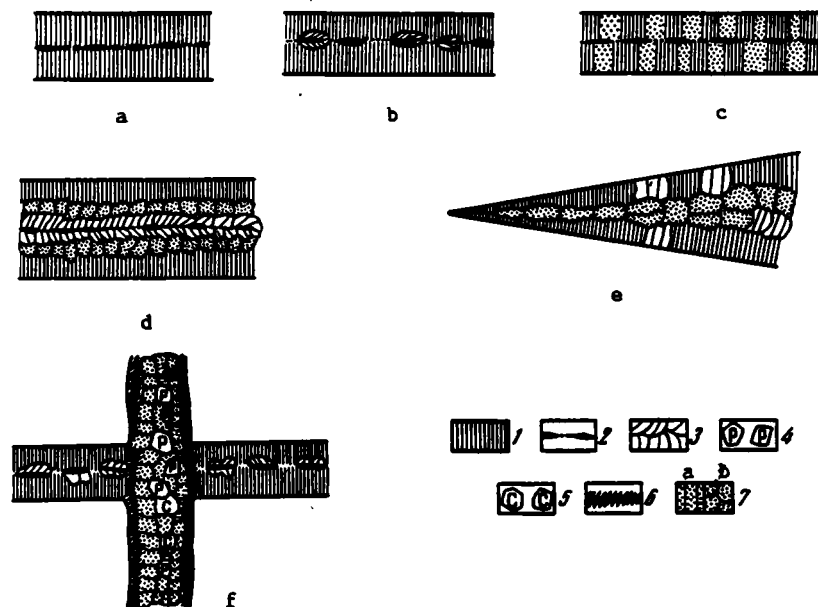


Fig. 2. Relative positions of gümbelite and companion minerals in veinlets: a) gümbelite veinlet with "middle cut"; b) mica plates growing over rock inclusions at the center of gümbelite veinlet; c) parallel growth of quartz-gümbelite aggregates in a veinlet; d) veinlet of a complex composition: gümbelite in salbands, mica plates, and quartz xenomorphs at center; e) wedge-shaped veinlet in a fragment of shungite II in breccia; f) relationship of horizontal gümbelite veinlet with a vertical (quartz-mica-pyrite-sphalerite) vein; 1) gümbelite; 2) rock inclusions; 3) lamellar mica; 4) pyrite; 5) sphalerite; 6) fine-lamellar micaceous aggregate; 7) quartz (a - lamellar, b - xenomorphous).

diagnosis by diffractional methods; 2) methodological investigations to study whether gümbelite and its mixes can be identified with dioctahedral micas of different polytype modifications and how reliably; and 3) determining the factors controlling gümbelite formation.

Carbon-containing rocks are widespread in the Lower Proterozoic of Karelia [3]. In the Transonega region (South Karelia) high-carbon rocks make up part of the Transonega suite, where they are interstratified with dolomite, siltstone, clayey schists, tuff, tuffite, and diabases. The Zazhogin shungite deposit is situated in the northeastern part of the Transonega Peninsula; it is confined to the upper subsuite of the Transonega suite. The Maksov placer at the center of the deposit concentrates most of shungitic rock reserves, with C_{org} over 20%. In the roof of the placer, different tuffs are interstratified; the underlying rocks are carbonate tuffs. Shungitic rocks are of a relatively even thickness in plan, except for swellings at cores of anticlines. The placer is 700 m long, 500 m wide, and 120 m thick. The chemical composition of shungitic rocks is peculiar. Two components are predominant: SiO_2 and C_{org} . Together, they account for up to 85%, with Al_2O_3 making up 5.5% and each of the oxides Na_2O , K_2O , CaO , MgO , and FeO accounting for at most 1.5-2.5%. Diffractometric investigations determined in shungitic rocks quartz, plagioclase, muscovite, biotite, chlorite, and apatite. In reflected light, pyrite, sphalerite, chalcopryite, pyrrhotite, and rutile were diagnosed. By structural features, shungitic rocks are subdivided into three varieties: stratified, present in minor amounts at the flanks of the placer; massive; and brecciated. Nine shungitic rock horizons are distinguished by thickness, average carbon content, and structural features. They are separated from one another by tuff, calcareous rock, and schist interlayers. Gümbelite is found in the sixth horizon amid brecciated varieties and in the ninth horizon, whose structure can be illustrated by bore holes 225 and 271.

At the top of the section in hole 225, there is a nearly 30-m member of diverse interstratified shungitic rock: shungites II, III, and IV, and dolomites with lyddite interlayers. The

TABLE 1. X-Ray Diffraction Pattern Data on Dioctahedral Micas* and Artificial Mixes

1M		2M ₁		2M ₂		2M ₁ + 2M ₂		2M ₁ + 2M ₂		2M ₂ + 1M ₁	
						2:1		1:1		2:1	
d/n	I	d/n	I	d/n	I	d/n	I	d/n	I	d/n	I
-	-	3.87	5	3.87	6	3.87	6	3.87	5	3.87	4
-	-	3.73	5	-	-	3.73	5	3.73	4	-	-
3.64	8	-	-	3.64	7	3.64	4	3.64	4	3.64	9
-	-	3.50	10	3.50	9	3.50	10	3.50	10	3.50	7
-	-	3.19	8	3.19	10	3.19	9	3.19	9	3.19	7
3.06	10	-	-	3.06	8	3.06	5	3.06	5	3.06	10
-	-	2.98	9	-	-	2.98	6	2.98	6	-	-
2.87	3	2.86	5	2.86	7	2.86	7	2.86	6	2.86	5
-	-	2.78	4	2.80	6	2.79	5	2.79	5	2.79	4
2.67	4	-	-	-	-	-	-	-	-	2.67	2

1M		2M ₁		2M ₂		2M + 1M ₁		2M ₁ + 1M		2M ₂ + 1M	
						1:1		2:1		1:1	
d/n	I	d/n	I	d/n	I	d/n	I	d/n	I	d/n	I
-	-	3.87	5	3.87	6	3.87	5	3.87	5	3.87	2
-	-	3.73	5	-	-	-	-	3.72	6	3.72	3
3.64	8	-	-	3.64	7	3.64	10	3.64	10	3.64	8
-	-	3.50	10	3.50	9	3.50	6	3.50	9	3.50	4
-	-	3.19	8	3.19	10	3.19	5	3.19	7	3.19	4
3.06	10	-	-	3.06	8	3.06	10	3.06	10	3.06	10
-	-	2.98	9	-	-	-	-	2.98	8	2.98	4
2.87	3	2.86	5	2.86	7	2.86	5	2.86	5	2.86	4
-	-	2.78	4	2.80	6	2.79	3	2.79	3	2.79	2
2.67	4	-	-	-	-	2.67	2	2.67	2	2.67	3

*Reflection intensities and spacings may vary slightly depending on mica composition.

latter's thickness does not exceed 0.5 m. Down the section, carbon-free calcareous tuffites give way to a member of interstratified shungite-containing carbonate rocks. A bed-shaped conformal metadiabase body is situated in the interval of 63-73 m. The section of bore hole 271 is similar. Top-to-bottom, one observes siltstone (20 m) and a member (40 m) of shungites IV, interstratified mainly with shungites II and III (and also rare lyddite interlayers), underlain by metadiabase.

In the interstratified member, a network of vertical and horizontal veinlets is well developed. The asbestos-like micaceous mineral (gümbelite) is found only in horizontal veinlets that coincide with the course of the layering. Their localization is confined to boundaries of rocks of different composition: shungites II and shungite-containing calcareous tuffites (Fig. 1c), shungites II-III (Fig. 1a), and less often layers of shungite II or III (Fig. 1). Investigations of cores determined that the veinlets are 0.5-5 mm thick and are shaped as flat lenses with no strictures. The contacts are sharp, with a transverse- or oblique-fibrous texture. Some veins are tens of meters long. Vertical veinlets across stratification are filled with 2M₁ mica and secondary amounts of quartz, well-crystallized pyrite, and sphalerite. They are wedge-shaped, elongate-lenslike, and clustery (see Fig. 1a), varying in thickness from 0.5 to 5 mm, up to 10 cm long, sometimes slightly meandering and interrupted, but with an overall consistent general orientation. Where shungite II disappears from the section, the rock becomes more massive and coarsely striated, and thin vertical veinlets disappear. We see in Fig. 1a, b that vertical veinlets either cross gümbelite veinlets or abut them.

In interlayers of shungite-bearing calcareous tuffites, situated lower in the section, horizontal veinlets of a morphology similar to gümbelite are filled with a biotite-phlogopite mica.

Gümbelite has also been found in shungite breccia. This peculiar rock has been described by us earlier [15]. According to the ratio of cement and fragments we distinguish strongly brecciated and medium-brecciated varieties with basal cement and slightly brecciated variety

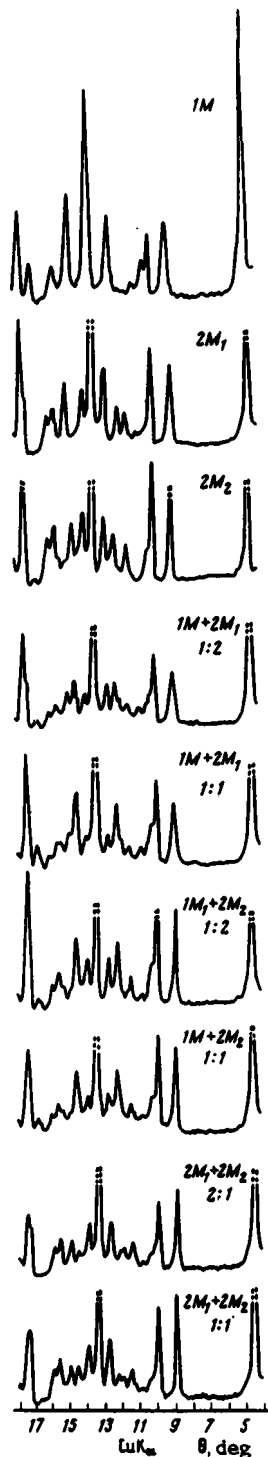


Fig. 3

Fig. 3. Powder diffraction patterns of dioctahedral micas and their mixes.

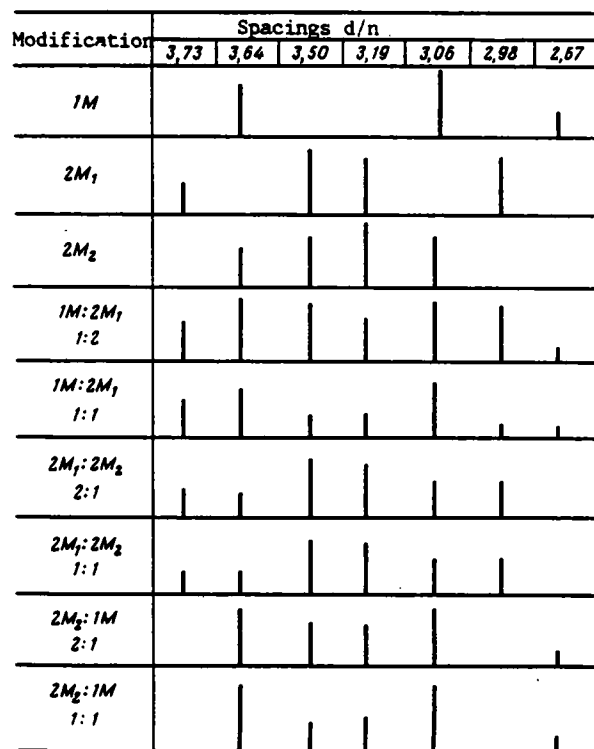


Fig. 4

Fig. 4. Distribution of intensities for a mix of polymorphous modifications of dioctahedral micas.

with veinlet-injection cement. Angular (sometimes cataclased) fragments are represented by shungite III or shungite II; gümbeelite is developed in these rocks in wedgelike veinlets. It is also found in veinlet cement in medium-brecciated black cement varieties.

Macroscopically, gümbeelite is a white, slightly greenish, soft, and oily asbestos-like material. The optical properties of the mineral have been described in [6]. An investiga-

TABLE 2. Unit Cell Parameters of Selected Specimens

Specimen number	Polytype	Unit cell parameters			
		a	b	c	β
8	2M ₁	5.22	9.04	20.14	96.1
	2M ₂	9.04	5.22	20.18	99.6
0.5/206	2M ₁	5.22	9.04	20.18	95.8
	2M ₂	9.04	5.22	20.18	99.6
14	1M (3T)	5.31	9.20	10.25	99.96
5	2M ₂	9.03	5.22	20.16	99.5

tion of gümbeelite veinlets in polished sections revealed the following: 1) gümbeelite either forms monomineral veinlets or occurs in association with other micaceous minerals and quartz; 2) in the middle of a veinlet a typical "middle cut" is observed, separating the veinlet into two layers; there are lenslike inclusions of carbon-containing rocks, measuring 0.02-1 mm, stretching parallel to the walls; 3) the elongation of gümbeelite fibers is perpendicular or slightly oblique relative to vein walls; the orientation of the micaceous mineral around inclusions is usually different from that observed near the vein boundaries; 4) two morphologic quartz varieties are distinguished - elongate columnar aggregates and xenomorphic rounded segregates - the former occur in parallel growths with gümbeelite, while the latter form one of the zones in polymineral fillings (Fig. 2c, d); they are also found in vertical veinlets; 5) tabellar mica in various quantities is associated with the "middle cuts" growing over rock inclusions (see Fig. 2b, e) that exhibit mainly uneven eroded contours; it also forms, together with gümbeelite, salbands of veinlets in breccia fragments.

General gümbeelite localization patterns were studied on specimens from Shunga, amply described in the literature [12, 13]. Two main features have been noted earlier as characteristic for a gümbeelitization zone [13]: 1) in diabase, dolomite, and shungite II sections, gümbeelite veinlets and zones stretching according to the course of surrounding rocks are found only in high-carbon rocks; and 2) in gümbeelitization zones, elongate pyrite lenslets are often found along the contact between shungitic schist and gümbeelite veinlets.

Our observations confirm that gümbeelite, both at Shunga and in the Zazhugin deposit, is confined to carbon-containing rocks, specifically to the parts where shungite II is present. Its characteristic feature is the ubiquitous development of two mutually perpendicular crack systems. There appears to be a correlation between these two facts: the spatial distribution of gümbeelite and the fissuring of shungite II [13]. The influence of the composition of the enclosing rocks is another important factor. It can explain, for example, why in the Zazhugin deposit, dolomites contain largely talc veinlets; diabases, biotite-chloritic veinlets; and shungite II, muscovite-fengitic veinlets.

The relationship between gümbeelite and pyrite is remarkable. Generally, pyrite is found in all Transnaga rocks in various forms. Syngenetic, primary-sedimentary, metamorphogenic, and hydrothermal mineralizations are distinguished according to genetic characteristics. At Shunga, the gümbeelitization zone exhibits fine insets and elongate lenses of primary sedimentary pyrite. Carbon-bearing pyritized rock impregnated evenly with gümbeelite occurs in a direct contact with shungite II; pyrite lenslets are also concentrated in it (see Fig. 1d). Many of them are skirted by gümbeelite veinlets; gümbeelite fibers are longer the thicker the pyrite segregates. These relationships clearly show that FeS₂ was developed earlier. On the other hand, disseminated gümbeelite and pyrite insets were formed probably almost simultaneously.

Micaceous minerals were studied by several methods: X-ray investigations, electron oblique textures, transmitted electron microscopy, and infrared spectroscopy. Most attention was paid to diagnosing 2M₂ mica in the presence of other polytypes. Oriented specimens were first prepared. All diffractograms of the specimens are characterized by an integer series of basal reflections with $d(001) = 10 \text{ \AA}$; the reflection $d(002) = 5 \text{ \AA}$ has a high intensity typical for Al-Mg dioctahedral micas. When treated with ethyleneglycol and glycerine and heated to 550°C, specimens displayed no shifts of basal reflections, indicating an absence of swelling layers in the mineral. The second stage of the study included an electron diffraction investigation, which can establish polytype mica modifications and distin-

guish them reliably. The results showed that, besides $2M_2$ micas, the specimens contained a certain amount of dioctahedral micas of different polytype modifications. This method has its limitations. First, it derives information from a very small quantity of material, which restricts the possible understanding of the phase relations in the specimens; secondly, it is less common than x-ray investigations. Accordingly, it became important to establish possible diagnostic criteria for determination of polymorphic phases in a mix.

For a long time, x-ray powder studies were believed to be insufficiently informative for phase diagnosis of a polytype mica variety because of a complete or partial overlap of spatial and basal reflections. However, Rusinova [11], following Sokolova [14], in studies of Debye powder patterns proved that $2M_2$ mica can be determined even in the presence of $2M_1$ mica.

Artificial mixes of micas of the polytype modifications $1M$, $2M_1$, and $2M_2$ of similar composition were prepared to study diagnostic criteria of gümbeelite. specimens were mixed mechanically in pairs in weight ratios of 1:1 and 1:2. Table 1 and Fig. 3 present diffraction patterns of the standard reference micas and their phase mixes. Pure dioctahedral micas of different polytypes are quite distinct. We will discuss the specifics of diffractograms of mixed specimens. In the diagnostic region (from 3.7 to 3.0 Å) they can be subdivided into two groups: one contains strong spatial reflections (for the polytype mixes $2M_2 + 2M_1$ and $2M_1 + 1M$); the other contains four reflections (for the mix $2M_2 + 1M$), except for the reflection with $d = 3.33-3.35$ Å, which overlaps with the basal reflection. The position of spatial reflections for a mix of polytypes of dioctahedral micas ($1M + 2M_1$) and ($2M_1 + 2M_2$) virtually coincides (see Fig. 3). The presence of a $2M_2$ mica is diagnosed from the strongest reflections with $d = 3.50$ and 3.20 Å. A similar diffraction picture ($1M + 2M_1$) is distinguished from the one just described by strong reflections with $d = 3.64$ and 3.06 Å. The second group, in case of a mix of $2M_2$ and $1M$ micas, has stronger reflections, with $d = 3.64$ and 3.06 Å, and weaker reflections, with $d = 3.50$ and 3.20 Å, as compared with the diffractogram of pure $2M_2$ mica. In addition, the presence of a $1M$ mica is also determined from the reflection 023 with $d = 2.67$ Å (Fig. 4). It is thus possible to test reliably in qualitative terms (and sometimes even in approximate quantitative evaluation) the presence of phase mixes of polytype modifications of dioctahedral micas.

The criteria were then used to study a series of micas from shungitic Karelian rocks and several specimens of micas from Donets Basin [2], provided kindly by L. G. Rekshinskaya.

The study showed the following. Gümbeelite is contained in veinlets parallel to stratification occurring in shungite II or on contact with it in vein cement of breccias [15], in veins on the fringes of shungite II fragments, and in black-cement breccia. All Karelian gümbeelite specimens, including the sample from Shunga, contain some dioctahedral $2M_1$ micas, while Donbass specimens contain $1M$ micas. The following regularity was observed in the proportion of polytypes of $2M_2$ and $2M_1$ dioctahedral micas: the wider a veinlet and the longer a gümbeelite fiber, the larger the quantity of mineral compared with $2M_1$ micas. The purest specimen was from Shunga, where the gümbeelite fiber length (l) was 2-5 mm; in specimens from breccia cement ($l = 0.5-0.7$ mm) dioctahedral $2M_1$ micas were predominant.

In horizontal veinlets permeating calcareous tuffites, a high-magnesium trioctahedral $1M$ (3T) mica was determined. Vertical veinlets cutting across gümbeelite-containing interlayers contained $2M_1$ dioctahedral micas.

The parameters of the unit cell of the micas studied, described in Table 2, are similar to those reported previously in the literature.

In [2], the hypothesis was advanced that the elongate needlelike shape in fibrous textures observed in a light microscope is a diagnostic feature of gümbeelite. Rekshinskaya investigated several specimens with electron microscopy. A virtually pure gümbeelite specimen (Table 3, specimen 5) consists of well-crystallized plank-shaped particles. Trioctahedral $1M$ (3T) mica is of a similar shape (see Table 3, specimen 4). Dioctahedral $2M_1$ mica consists of platelike isometric particles. A specimen consisting of a mix of mica polytypes (see Table 2, specimen 8) includes both long and platelike particles. The data indicate (see Table 2 and Fig. 2d) that the former probably belong to gümbeelite and the latter to $2M_1$ micas.

Table 3 presents chemical analysis data and compositions of gümbeelites from different carbon-bearing rocks. The cation ratios of gümbeelite 2:1 layers exhibit a wide Si-for-Al isomorphism in tetrahedral frameworks, ranging from 0.52 to 1.08 f.u. Aluminum is the main octahedral cation; in most instances, it is slightly substituted by Mg and Fe^{3+} cations. A slightly higher Mg content (0.42 f.u.) is recorded for the Shunga gümbeelites. This may be

TABLE 3. Chemical Composition of Micas

Component	Specimen number													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
SiO ₂	52,5	49,71	50,00	50,52	49,54	49,35	48,71	48,78	49,52	56,12	45,38	45,88	44,0	41,28
TiO ₂	1,0	1,04	—	—	0,87	0,66	0,62	0,86	0,81	0,06	—	—	—	0,46
Al ₂ O ₃	29,50	28,62	36,45	31,04	29,51	29,20	29,10	28,54	25,06	26,79	38,04	38,04	37,95	14,90
Fe ₂ O ₃	3,50	2,69	0,37	3	—	0,86	0,82	0,64	1,36	3,28	0,40	0,46	2,25	4,88
FeO	—	—	—	—	0,70	—	—	—	0,56	—	—	—	—	—
CaO	—	—	—	—	0,25	0,54	0,16	0,10	0,27	0,95	—	—	0,56	—
MgO	1,16	1,60	0,45	1,88	4,14	4,14	4,75	2,80	2,88	1,48	—	—	0,32	23,43
K ₂ O	5,06	6,80	5,01	3,18	8,21	8,80	8,35	7,22	6,47	4,41	7,44	7,53	7,53	7,19
Na ₂ O	—	2,21	—	—	0,35	—	—	0,18	0,28	—	0,54	0,48	1,15	0,08
MnO	—	—	—	—	—	0,01	0,01	0,04	—	—	0,13	0,36	—	0,04
H ₂ O ⁺	7,75	7,38	7,96	7,0	6,56	5,76	6,23	—	7,08	6,87	7,38	6,53	6,20	5,99
H ₂ O ⁻	—	—	—	—	0,24	0,01	0,40	—	0,45	—	0,61	0,41	—	0,23
calc. loss	Not det.	Not det.	Not det.	1,46	Not det.	—	—	—	—	Not det.	—	—	—	0,86
CO ₂	—	—	—	—	—	0,30	0,25	—	—	—	—	—	—	—
Σ	100,47	100,05	100,22	98,08	100,37	99,72	100,20	—	—	100,0	99,92	99,69	99,96	99,34
Ion:														
Si	3,480	3,377	3,260	3,386	—	3,314	—	3,399	3,53	3,66	3,05	3,06	2,94	2,95
Al ^{IV}	0,522	0,623	0,740	0,614	—	0,686	—	0,60	0,47	0,34	0,95	0,94	1,06	1,05
Al ^{VI}	1,780	1,669	2,060	1,837	—	1,625	—	1,75	1,63	1,72	2,05	2,05	1,93	0,20
Fe ²⁺	0,174	0,137	0,018	0,151	—	0,043	—	0,033	0,07	0,16	0,02	0,02	0,11	0,26
									0,03 ⁺					
Mg	0,115	0,162	0,044	0,188	—	0,425	—	0,291	0,31	0,120	—	—	0,03	2,49
Mn	—	—	—	—	—	—	—	0,002	—	—	0,01	0,02	—	—
K	0,427	0,589	0,411	0,271	—	0,730	—	0,643	0,59	0,370	0,64	0,64	0,64	0,65
Na	—	0,291	—	—	—	—	—	0,02	0,04	—	0,07	0,06	0,15	0,01
Ca	—	—	—	—	—	—	—	0,007	0,02	—	—	—	0,04	—

Notes. Sampling site: 1) Grafenthal, Thuringen Forest [21]; 2) Moutier [21]; 3) Moutier [21]; [4] Nordhalben, Franconian Forest [19]; 5) Shunga, Karelia [12]; 6, 7) Shunga [13]; 8, 9) Zazhagin deposit, sites 225 and 271; 10) Gorlov basin [2]; 11, 12) Donbass [4]; 13) Donetsk Basin [17]; 14) Zazhagin deposit, site 225. Specimens 6, 8, 9, 10, and 13 are polytype mixes: 6 - (95% 2M₂ + 5% 2M₁), 8, 13 - (50% 2M₂ + 50% 2M₁), 9 - (70% 2M₂ + 30% 2M₁), 10 - (70% 2M₂ + 30% 1M). In specimen 8 water was not determined because of scarcity of material; in specimen 9, additionally, these contents were determined: C - 3.55% and S - 0.93%.

the result of nearby occurrence of dolomite rocks. All gümbeles have a low content of interlayer K^+ cations due to a low charge of 2:1 layers compared with true micas. An excess positive charge in octahedral frameworks is sometimes observed at a general content of octahedral cations above 2 f.u. (see Table 3). In [1] it was demonstrated that gümbeles may contain NH_4 -groups functioning as an interlayer cation. A chemical analysis of these groups is difficult, but ammonium groups can be diagnosed by IR spectra of these minerals. An absorption band with a peak near 1430 cm^{-1} in IR spectra of specimens 5, 8, 9, 10, and 14 suggests the presence of NH_4 -groups in mica interlayers [20]; along with K^+ cations, it partially compensates for the deficit in the charge layer. For comparison, IR spectra of two specimens of dioctahedral $2M_2$ polytype micas were taken. The specimens were extracted from gold vein deposits described in [11]. They have no NH_4 -groups.

We will discuss these results. Gümbeles has been determined in Zazhagin shungite deposits in quasiconformal horizontal veinlets in shungite II sections and in black-cement shungite II breccia. Dioctahedral $2M_1$ mica is present in different proportions together with gümbeles. All gümbeles specimens contain an ammonium group.

What were the formation conditions of these gümbeles veinlets? Answering this question is difficult, for one thing, because of a lack of experimental data. No experimental study with hydrothermal muscovite synthesis has diagnosed a $2M_2$ polytype. In a natural environment, the benchmark for estimating the temperature of coal-containing rock metamorphism in which gümbeles veinlets occur in this case is the degree of graphitization of carbon matter. It is characterized by thermal parameters (T_{in} and T_{max} of exoeffect), the layer spacings $d(002)$, optical reflection spectra, and elemental composition (C, H, and N):

$d(002)$ Å	T_{in} , °C	T_{max} , °C	αR_{max}	$\Delta R_{0.5}$	C	H	N
3.430	480	650	2.4	1.8-2.4	97.2	0.8	0.5

These data determine a temperature interval of $320-350^\circ\text{C}$ [16]. These conditions are not specific for certain locations, but apply to the entire Zazhagin deposit. The hypothesis advanced in [13] that additional heating at the expense of diabases is needed for gümbeles formation does not appear plausible, because their influence on enclosing rocks does not reach further than 10-15 cm from the contact, and there is no gümbeles in these zones.

X-ray investigations of veinlets with gümbeles showed Karelian specimens to contain $2M_2$ dioctahedral mica, and Donbass specimens to contain 1 M mica, besides $2M_1$ mica. One can tentatively assume that the gümbeles existence region corresponds to a temperature interval of the transition of 1M Al-Mg mica to $2M_1$; according to experimental data, this takes place when the temperature rises from 250 to $300-350^\circ\text{C}$ [10]. Several experiments, kindly conducted for us by Mukhamet-Galeeva, indicated a relatively broad field of temperature stability of Karelian gümbeles: the natural specimen kept in an autoclave for 3 weeks at $T = 650^\circ\text{C}$ and $P = 3$ kbar experienced no structural change.

The authors have no criteria for estimating the role and magnitude of pressure in gümbeles formation, but it is known that it did not exceed 3 kbar in the Onega trough. Previously, it has been noted for other areas of gümbeles occurrence that it is commonly found in schistose and strongly dislocated strata [2]. This seems to indicate that gümbeles should be widespread in black schist formations of low degrees of metamorphism, such as in the Baltic Shield, or carbon-containing rocks of the Pechenga series, but no such data are available as yet.

Diffraction studies determined the presence of dioctahedral $2M_1$ Al-Mg mica in gümbeles veinlets. Relationships of $2M_1$ and $2M_2$ polytypes in horizontal veinlets are quite complex. Several hypotheses can be considered. One mechanism of gümbeles growth is geometric selection, with the mineral filling cavities formed by contraction of shungite rocks during diagenesis [13]. An alternative explanation assumes that a parallel-fibrous gümbeles aggregate grew in closed cracks, developing a force strong enough to spread apart the crack walls and overcome the lithostatic pressure. The wider a veinlet, the longer the gümbeles fiber, and the smaller the $2M_1/2M_2$ quantitative ratio; $2M_1$ mica is predominant in the narrowest veinlets. There are no definitive data to determine which of the polytypes is primary. Assuming that gümbeles exists only in asbestoslike form and that $2M_1$ mica is platelike, we can conclude that, regardless of the growth mechanism, $2M_1$ mica was formed before gümbeles, because its plates are confined to salbands of veinlets or to inclusions at their centers.

A comparison of the compositions of different veinlets and their positions in space shows that, initially, gümbeles was deposited in horizontal cracks together with quartz. Later,

as hydrothermal mineralization conditions were changed, dioctahedral $2M_1$ mica was formed in cross-cutting vertical cavities together with well-crystallized pyrite.

Unlike other regions where gümbelite is found in diverse rocks of coal-bearing strata (sandstones, siltstones, argillites, and carbonitized rocks [2]), the mineral in Karelia is localized in shungites II or near them. A specific feature of shungites II is an extremely high (up to 70%) C_{org} content, apparently responsible for the physical characteristics of these rocks and their capacity for a considerable volumetric reduction by carbonization of organic matter, that would leave it susceptible to cracking and subsequent filling of cracks with gümbelite. The localization of gümbelite around pyrite lenslets [13] can also be connected with the favorable conditions provided by cavities formed when the volume of sedimentary pyrite shrank during diagenesis.

The composition of surrounding rocks affected micaceous minerals. In particular, veinlets in sections of shungites II, III, and IV contain dioctahedral Al-Mg micas; in calcareous tuffites they contain high-magnesium 1M (3T) mica. A common trait of all these micas is the presence of NH_4 -groups in interlayers as a characteristic feature of mineral formation settings.

* * *

Methodological study has made it possible to diagnose reliably from x-ray powder patterns of preparations the presence of dioctahedral $2M_2$ mica in a mix with $2M_1$ and 1M micas. In all horizontal veinlets studied, gümbelite, as well as dioctahedral $2M_1$ mica, has been determined in certain parts of the section. The wider the veinlet, the higher the gümbelite content in it.

Geological observations, and polished sections and x-ray investigations have suggested the following sequence of $2M_1$ and $2M_2$ mica formation. First, horizontal cracks around inclusions of coal-containing rocks were opened, and $2M_1$ mica was formed. The veinlet was then filled with gümbelite; dioctahedral $2M_1$ mica was formed in vertical veinlets cutting across gümbelite veins.

The main factors that controlled gümbelite formation included both physical features of rocks (shungites II), which determined cracking, and chemical characteristics responsible for the source of the material for the veins. The presence of NH_4 -groups in the mica structure is associated with rock composition.

A special experimental investigation will be necessary for describing the P-T conditions of gümbelite formation.

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SOURCES OF ORE-FORMING ELEMENTS IN MODERN HOT SPRINGS OF THE OCEAN FLOOR*

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In our report, we critically examine the position put forward by G. Yu. Butuzov concerning the role of magmatic fluids in hydrothermal-sedimentary oceanic lithogenesis.

The question as to the sources of ore-forming solutions and ore matter has major significance for understanding the origin of pyrite deposits and is widely discussed in the geological literature. Thorough reviews of this question are presented in [9, 19], in particular. One of the most important problems involved is the ratio of ore metal fractions brought from the magmatic chamber by means of fluid separated from the melt (a juvenile, "magmatic" source) and leached from the rocks of the underlying ore shoot during convective circulation of surficial waters, including seawater (recycling). The interest of geologists in the modern hydrothermal springs of the ocean is, to a significant degree, connected with the hope of answer to this question based on data from the study of active ore-forming systems.

The recycling idea is accepted in the articles of almost all investigators of hydrothermal springs in the modern ocean. Until recently, however, there were no overviews of the research in which all arguments concerning the source of the material in hot springs were presented in turn and discussed in detail. The series of two articles published by G. Yu. Butuzov [2, 3] is essentially the first such overview. The evidence presented in this report

*In connection with the report by G. Yu. Butuzov, "The problem of sources of material in hydrothermal-sedimentary oceanic ore genesis," Reports 1 and 2, Litol. Polezn. Iskop., Nos. 5 and 6 (1986).

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TABLE 1. Comparison of the Compositions of Ocean-Floor Hot Springs with Solutions in Experiments on "Seawater-Basalt" Interaction

Object	Content, mg/kg				pH, °C
	Mn	Fe	Cu	Zn	
East Pacific Rise 21° N [43]*	38-53	42-136	0,6-2,8	5,8-6,9	3,3-3,6
Experiment [40]†	66	485	1,4	7,9	3,3

*Extrapolation for a pure hydrothermal solution ("end-member") for the OBS, SW, and HG fields (see also [3], Table 2).

†Experiment with East-Pacific-Rise basalt at 400°C, 40 MPa; water/rock = 1; duration, 579 h.

indicates that the principal source of H₂O and Cl in hot springs is seawater. The composition of the solution with respect to petrogenic elements (including Fe and Mn) is formed as a result of the interaction of seawater with basalt; sulfur has a special source (seawater + basalts).

In [3], it is concluded that chalcophile ore elements (Cu, Zn, Pb, etc.) arrive at the hot springs primarily within the fluid phases of magmatic melts (as do gaseous compounds, i.e., H₂, He) and that the role of leaching of basalts in this process is minor. It is important to note that this conclusion is based upon an interpretation of indirect geological-geophysical information. Direct geochemical criteria (chiefly isotopic) widely used in geology to solve problems connected with a source of material, as correctly pointed out by G. Yu. Butuzov, does not allow one to distinguish between transport of elements from the melt via fluid and leaching of the elements from basalts, since basalts inherit the isotopic composition of the melt (with respect to S, Pb, Sr, and even C and He). Data existing at present allow us to evaluate a number of aspects of the problem under consideration differently and to enter a disagreement with the conclusion of G. Yu. Butuzov. This compels us to analyze the argument presented in articles [2, 3].

The denial of a significant role to leaching processes in the case of ore-forming metals (except for Fe and Mn) is based upon the following assertions [3]: 1) results of experiments on the interaction of seawater with basalt (obtained by various authors); these results are contradictory, equivocal, and do not clarify the behavior of the metals during hydrothermal leaching; 2) in ancient analogs (pyrite deposits), there are no signs of removal of ore elements from the surrounding rocks; 3) it is difficult to interpret the geochemical specificity of sulfide ores in the ocean on the basis of a hydrothermal-leaching process. These assertions will be examined in more detail.

Experiments on the Interaction of Seawater with Basalt. G. Yu. Butuzov correctly points out that it is impossible to obtain reliable data on the behavior of Cu when using gold ampules and the components of the sampler in Dickson hydrothermal units. Actually, the Cu leached from the basalts in this case is immediately absorbed from solution by the walls of the ampule, along with the formation of an Au-Cu alloy [39]. However, as described in a recently published report [40], experiments have been carried out in an apparatus made entirely from titanium. These experiments show that Cu accumulates in solution in concentrations of up to 1.4 mg/kg, concentrations comparable with the concentrations in the hot springs of the East-Pacific Rise (EPR) at 21°N.

The discrepancy noted by G. Yu. Butusova [3] between the research of J. Bischoff and F. Dixon [25] in which Ni accumulated in solution (carried out in 1975), and subsequent reports, where such accumulations were not present, is connected with methodological error [25]. One of the details of the set-up was that the end of the sampler was made out of stainless steel, which contaminated the solution with nickel; this detail lead to a replacement with titanium in subsequent research [39].

The variety of experimental data (more than 20 experimental reports have been published thus far), diagnosed in [3] as lack of clarity and conflicting results, is connected not nearly so much with a lack of reproducibility of the experiments as with the fact that the experiments reveal a dependence of the behaviors of ore elements upon several factors at one time. The chief factors among these are the composition of the rock, the composition of the original solution, the temperature, the water-rock ratio, and the duration of the interaction

TABLE 2. Ratio of Elements (average geometric values) in Basalts, Hydrothermal Solutions, and Ores of the Ocean Floor (according to data presented in [3])

Object	Cd/Zn	Ag/Zn	Pb/Zn
Tholeiitic basalts	0,00164	0,00038	0,0256
Hydrothermal solutions, ERP, 21° N, (samples 1-3)* n = 3	0,00275 (0,00252- -0,00297)†	0,00055 (0,00048- -0,00059)	0,0089 (0,0069- -0,0109)
Sulfide ores, East Pacific Rise and Juan de Fuca Ridge n = 10	0,0019 (0,0003- -0,01)	0,00056 (0,0002- -0,0024)	0,011 (0,003- -0,12)

Note. n is the number of samples.

*Sample 4, inferred on the basis of Cu and Ag contents; a portion of the ore components were already lost and therefore were not taken into consideration.

†Ranges of values are presented in brackets.

(for a review of the experimental data, see [38]). In a recently published article [43], it was shown that pressure exerts a substantial influence upon the behavior of ore elements at temperatures of 350-400°C. In experiments carried out at a pressure of 40 MPa, solutions were obtained which were very similar to the hot springs of the East Pacific Rise at 21°N (Table 1) with respect to metal content and other parameters.

Evacuation Aureoles in Ancient Objects of Similar Nature. During special investigations undertaken on the Ural copper-pyrite deposits, broad evacuation halos of ore elements were discovered on the flanks of the deposits [1, 13]; in addition, evacuation halos were recently detected under deposits at Cyprus [37].

Connection between Metal Content in Basalts, Thermal Solutions, and Sulfate Ores. For the example of the contrasting behavior of Ni and Cd (Ni is plentiful in basalts, but present in small amounts in sulfide ores; the situation is just the reverse for cadmium), it is asserted, "it is difficult to interpret the geochemical specificity of thermal solutions and ore accumulations on the ocean floor from the standpoint of the leaching concept ... in general, it is important to emphasize the complete absence of a connection between the contents of metals in the basalts of the spreading zones and the contents of metals in the sulfide formations of the ocean floor" [3, pp. 9-10].

If one considers elements similar with respect to migration forms within a hydrothermal solution and possessing similar properties when deposited in the form of sulfides, then a geochemical connection between ores and basalts can easily be detected. We will demonstrate this using the ratios of contents of the geochemically similar elements Cd/Zn, Ag/Zn, and Pb/Zn as an example. These ratios (Table 2) were calculated according to data presented in [3] for the most studied research object, the hydrothermal springs of the East Pacific Rise at 21°N. They show that, despite the large scatter of values for the ores, the average values in the hydrothermal solutions and ores are very similar to the ratios in basalts. For other chalcophilic elements, for example Cu and Hg, the constant ratio was disturbed as a result of a separation of elements during the course of ore deposition. The relationship between the ratios Cu:Zn:Pb in ancient pyrite ores and the enclosing volcanites is well known [7]. It has been discovered within the modern ocean in sulfides of hydrothermal origin [12]. A similarity of factors associated with the concentration of ore/basalt was noted in [26] for the group of elements Zn-Pb-Ag-Cd and Cu-As-Hg-Mo-Ge-Tl-Au.

The nature of the contrasting behavior of nickel and cadmium described in [3] is fairly evident. Cadmium is an analog of zinc and forms stable chloride complexes similar to those of zing. Therefore, during hydrothermal leaching, Cd, together with Zn, will be easily extracted from basalts and will be easily transported by solution; also, zinc sulfides will capture Cd in the form of an isomorphous admixture during sedimentation of the ores. Nickel is the weakest complex-former within the group of elements Mn, Fe, Ni, Co, Cu, and Zn [6].

TABLE 3. Estimate of Portion of Magmatic Fluid Necessary According to "Melt-Fluid" Distribution Coefficients

Element	K_p [21]	Content, mg/kg			Portion of magmatic fluid necessary in composition of the hydrothermal solution, %
		in basalt [3]	Limiting estimate for fluid according to K_p	in hydrothermal solutions of the East Pacific Rise 21° N [43]	
Cu	5	81	405	0,6-2,8	1
Zn	0,5	78	39	5,8-6,9	15-18
Pb	0,45	2	0,9	0,04-0,07	4-8

When the content of chloride is equal to that of seawater, Ni is present in the form of a free water ion [6] over practically the entire hydrothermal range of temperatures and does not make complex chloride forms which would increase its migrational capability. At the same time, Ni emerges as an analog of Mg and Fe [26] in mineral basalts and their metamorphic varieties and is very intensively captured by chlorites, serpentine, and other secondary magnesian minerals. This is responsible for its low mobility during leaching and, consequently, for its low content in sulfide ores. Therefore, the separation of Ni and Cd during hydrothermal leaching is entirely predictable.

Thus, there isn't a single consideration discussed in [3] which involves major objections to the hypothesis of hydrothermal leaching of ore elements from basalts.

An argument in favor of a magmatic source, i.e., the arrival of ore components with magmatic fluids, was put forward in [2, 3] for an interpretation of geological-geochemical data which can be divided into two groups: 1) the tectonic positions of the hydrothermal vents; 2) the magnitude of the heat flow; 3) the quantity of volatile components in the magmatic melts; 4) the coefficients for the fractionation of elements between fluid and melt; 5) the composition of the magmatic fluids.

Tectonic Position of the Hydrothermal Vents. It was demonstrated in [3, p. 11] that the localization of high-temperature hydrothermal systems is controlled by deep faults and the corners where such faults intersect, "where intermediate magmatic foci arise in connection with transcrustal zones along which mantle melts and flows of volatiles separated from such foci periodically penetrate." However, in 1982 R. Ballard and Zh. Fransheto [24], analyzing the distribution of hydrothermal fields known at that time for the East Pacific Rise and the Mid-Atlantic Ridge, showed that the fields coincide with uplifted summit regions of the mid-oceanic ridges (MOR) which were, as a rule, furthest away from transform faults. The results of new research revealed the necessity of taking into account smaller breaks in the continuity of the ridge axes as well as transform faults, but, in general, gave positive support for the previously discovered pattern [29, 33]. A spatial connection between the hot springs and zones of intersection of the rift axis by transform faults has been found only in the case of the Red Sea. The specifics of this case are connected with an important peculiarity of the hot springs of the Red Sea: the presence of brines (hot metalliferous and cold nonmetalliferous) heavier than seawater. The brines accumulate here in basins of the rift axis and gravitate toward the transform faults.

The absence of a relationship between the high-temperature hot springs in the ocean and transform faults indicates that separation of volatile flows from the mantle (without penetration of the melt) in itself apparently does not lead to active hydrothermal activity at the MOR.

Magnitude of the Heat Flow. To substantiate the emergence of deep fluids, a quote from a monograph by V. I. Kononov is presented in [3]: "The heating of these systems cannot be accounted for by a focus of conductive regional heat flow alone," and "an additional flux of deep heat is required, a flux connected either with conductive heating from shallow-lying magmatic foci or from the emergence of a steam-and-gas fluid" [8, p. 35].

The conclusion asserting the necessity of an inflow of a deep fluid cited in the report of V. I. Kononov involved the example of the heat-carrier in the hot springs of Reykjanes Cap (Iceland), where no near-surface magmatic chamber has been located [8, p. 75]. On the MOR, the existence of near-surface (on the order of 1-2 km) vents for roofs of magmatic foci under ore-forming hydrothermal systems was established by a combination of geophysical methods [32], and, consequently, the flow of a deep-carrier is no longer unrequired. Actually,

TABLE 4. Estimate of Portion of Magmatic Fluid Necessary according to Composition of Gas-Condensates of the GTFE

Element	Content, mg/kg		Portion of magmatic fluid necessary, %
	in hydrothermal solution of the ERP, 21° N [43]	in gases of the GTFE [11] (average values)	
Cu	0,6-2,8	6,4	9-44
Zn	5,8-6,9	33	18-21
Ag	0,0028-0,0041	0,0034	> 82
Cd	0,016-0,020	1,07	1-2
Pb	0,04-0,074	1,42	3-5
Co	0,004-0,013	0,018	20-72

calculations carried out by many authors indicate that the necessary magnitudes of heat flow can be consistently explained without the participation of magmatic fluids [28, and others]. This does not contradict the conclusion from [8] presented above.

Quantity of Volatile Components in Magmatic Melts. In [2], G. Yu. Butuzova placed doubt upon the low estimates of H₂O content in the primary magmas of the East Pacific Rise (0.1%,* according to P. Uilli) and, manipulating the data presented in [14, 16], suggested that the original magmas of the East Pacific Rise contain much more water (several percent). On this basis, Butuzova hypothesized that the 0.3-0.4% water content in the tholeiitic basalts of the MOR and Red Sea are the result of a removal of fluids during the crystallization of the magmatic melts.

The numerous studies of the contents of volatile components now available convincingly show that basaltic melts formed at the MOR are substantially more depleted of volatile components than the melts of the active oceanic margins [20]. Taking this into account, the data of G. Yu. Butuzova is not representative of the magmatic melts of the MOR. The estimate [16] is applicable only to the basalts of the mobile belts, i.e., to regions of ancient oceanic margins. The Troodos ophiolite complex, samples of which have been studied by A. V. Sobolev and V. B. Naumov, also represents a fragment of crust formed in an oceanic-margin environment [15].

The ferrobasalts of the Sikeiros fracture (Pacific Ocean) studied by I. D. Ryabchikov et al. [14] belong to a type of basalt encountered relatively rarely on the MOR. According to data from petrological studies [40], they are the result of a deep fractionation of tholeiitic melts which took place under conditions involving small, isolated magmatic bodies (types of sills and dikes). Such a degree of fractionation is not reached under conditions involving large bodies. During crystallization differentiation of the tholeiitic melts, the water behaves as an incoherent component and accumulates in the residual melt. As studies of volatile components in ferrobasalts and andesites of the Galapagos Rift indicate [27], the concentration of H₂O can reach 1.5% under these conditions when the original concentrations were 0.1-3%. In [2], two different concepts used in [14] are combined, that of a "primitive parent melt" (i.e., prior to differentiation) and that of a "melt prior to the beginning of the crystallization of ferrobasalt," (i.e., a melt having undergone crystallization differentiation in the focus). The value of 1.5-3% put forward by A. G. Butuzova applies to dedifferentiated melt, and, apparently, could not be present in all of the basaltic melts of the MOR.

A large quantity of data now exists concerning the water contents in the chilled glasses of ocean-floor basalts. These data provide more reliable information on the properties of melts [22]. The water concentrations amount to 0.1-0.4% in all. An interpretation of the data (this included taking into account the isotopic ratios of hydrogen stabilized by degassing processes [42]) leads to an average water content in the parent magmas on the order of 0.2% [30, 31, 42]. At such a low water content, the magmas of the MOR are not completely saturated with respect to water vapor under conditions involving intermediate foci [22] and, therefore, a separation of essentially aqueous fluids is impossible here. Actually studies of the composition of gas inclusions in the basalts and basaltic chilled glasses of the MOR

*Here and further along, the quantity of water is expressed in weight percentage.

indicate that they are filled with almost pure CO_2 [23, 35, etc.]. When one succeeds in determining the water content within the inclusions in such cases, the water content amounts to less than 3-6%. The data obtained is in agreement with the results of a theoretical analysis [22] according to which the magnitude of $\text{CO}_2/(\text{CO}_2 + \text{H}_2\text{O})$ is greater than 0.95 for pressures above 0.5-1 kbar (this corresponds to depths of 1-3 km for intermediate magmatic chambers). These data indicate that the water removal from the fluid composition during degassing of the melt is relatively minor. It is important to note that, in contrast to basaltic melt, the fluid has an essentially carbonic-acid composition.

Coefficients for Fractionation of Elements between the Fluid and Melt (K_D). On the basis of the experimental investigations of I. D. Ryabchikov, N. I. Khitarov, S. D. Malinin, and others, it was demonstrated in [3] that leaching from magma and transport of the ore elements in water-chloride fluids was possible. There is no reason to object to such a qualitative solution to the problem. For the problem of the relationship between sources of metals, however, it is important to have the type of quantitative estimate absent in [3]. The reason for this is understandable: almost all of the published data for K_D in a "melt-fluid" system are applicable to melts of an acidic (granitic) composition [10, 21]. Moreover, the salt compositions of fluids separated from melts on the median ridges is unknown. Under these conditions, even semiquantitative, limiting estimates are important to obtain.

Data on the K_D of the petrogenic elements among basaltic melts and aqueous fluids of various compositions were recently published by N. S. Gorbachev [5]. The values are one-two orders of magnitude lower than for granitic melts according to a report [10]. Although direct comparisons of the data are impossible (experiments at different temperatures and differing fluid compositions), the results allow one to use the K_D of a "granitic melt-fluid" as an upper limiting estimate. If one takes into consideration that the fluids of the MOR have CO_2 as a principal component (which lowers their extracting capability), then the reliability of such a choice is increased.

By using the K_D values from [21], we can calculate the limiting content of metals in the fluid on the basis of the content of Cu, Zn, and Pb, and then, by comparing these values with the contents of these metals in the hydrothermal springs of the East Pacific Rise, we can estimate the necessary portion of magmatic fluids. From the data presented in Table 3, it is evident that, from the point of view of the K_D , the portion of magmatic fluid should be not less than several percent of the hot springs of the EPR in order to provide their observed metal-carrying capability.

Composition of the Magmatic Fluids. This problem is solved in [3] on the basis of an analogy with the gas-condensates of the Tolbachik Volcano [11]. Assuming that they are geochemically similar to the composition of thermal solutions and sulfide ores of the ocean, G. Yu. Butuzova hypothesized that the fluid source of the metals plays an important role in hydrothermal-sedimentary ore genesis.

It must be noted that a similar analogy is not entirely correct here: the solid products of the Great Tolbachin Fissure Eruption (GTFE) are petrologically similar to the basalts of the oceanic islands rather than to the basalts of the MOR [18]. Water vapor (H_2O 83.5% and CO_2 5.55% [11]) sharply predominates in the volcanic gases of the GTFE; this also associates them with the volcanism of the oceanic islands, since the ratios of H_2O and CO_2 are directly opposite in the volcanic gases of the GTFE. This should be strongly reflected in the transport of ore elements. But even if such an analogy is admissible, a very substantial participation of fluids of the "Tobachin-type" would be required to provide the necessary metal-carrying capacity of the East Pacific Rise hot springs, as simple a calculation shows (Table 4). The portions of the principal ore elements, Cu and Zn, would amount to tens of percents.

Thus, the analysis of the data used in [2, 3] indicates an absence of rigorous evidence for large-scale emergence of magmatogenic fluids at the surface in the case of the MOR. At the same time, the minimum necessary portion of these fluids should equal $n \cdot 10\%$ in order to provide the observed metal-carrying capacity of the East Pacific Rise hot springs with respect to Cu, Zn, Ag, and Pb (not to mention Fe and Mn). Similar quantities could be reliably identified by isotopic methods.

Thus, the key feature in determining the role of magmatogenic fluids in hydrothermal ore genesis becomes the relationship of such fluids to the seawater circulating in the hydrothermal system. Even an estimate of the limiting, maximum possible contribution of magmatic fluids to the system turns out to be sufficient for deciding the basic question of what is "important vs unimportant" in this case. It is possible to arrive at such a limiting estimate by various paths.

The portion of magmatogenic fluid can be evaluated by comparing the separation of volatiles from the mantle with the flow of water in the hydrothermal systems of the mid-oceanic ridges. The first value, according to the theory of Earth evolution proposed by O. G. Sopokhin, amounts to almost 10^{14} g/yr [4, pp. 146-147]. The calculation of the quantity of water arriving at the mid-oceanic ridges from the mantle carried out in [30] on the basis of the contents of H_2O in basaltic melts yields a similar value of $(1.1 \pm 0.3) \cdot 10^{14}$ g/yr. A somewhat larger value, $5 \cdot 10^{14}$ g/yr, was reported in [17]. The global flux of water passing through the hydrothermal systems of the MOR has been calculated by many authors, and the values obtained are within a range of 10^{17} - 10^{18} g/yr [41]. The indeterminacy within an order of magnitude is connected with the fact that the average temperature of the water being discharged is unknown. The minimal volume (10^{17} g/yr) was obtained for the highest (350°C) temperature.

It follows from these values that the portion of magmatogenic components in the hydrothermal springs cannot exceed 0.1-0.5%. This estimate is probably exaggerated, since it involves the assumption that all of the water separated from the mantle leaves the rock and arrives at the hot springs. It is also assumed that all of the hot springs are very hot (350°C). At the same time, the estimate is global in character and can exclude local variations.

One of the principal features of the fluids removed from the basaltic melts of the MOR is their essentially carbonic-acid composition. This allows us to use CO_2 as a "geochemical marker" for determining the possible involvement of magmatogenic fluids in the composition of the hydrothermal springs of the ocean floor. The quantity of CO_2 in the hydrothermal solutions at 21°N of the East Pacific Rise amounts to all of 5.72 mmole/kg (or 0.025 mass %) [44]; for 13°N, it equals 10.8-16.7 mmole/kg (or 0.05-0.07 mass %) [34]. Taking into account the content of other components, this corresponds to a portion of magmatic fluid equalling 0.03-0.1%. This value apparently exceeds the original portion of fluid, because CO_2 can get into the hydrothermal solution from other sources besides the seawater circulating in the system and washing gases from the basalts.

From a comparison of the values obtained with the data in Tables 3 and 4, it is evident that the maximum possible portion of magmatogenic fluids is one to two orders of magnitude lower than the minimum necessary to provide the observed metal-carrying capacity of the MOR hot springs. At the same time, as indicated above, the hypothesis of a hydrothermal leaching of metals from basalts allows for a consistent description of the results obtained.

Therefore, it is impossible to agree with the conclusion of G. Yu. Butuzova concerning the leading role of magmatogenic fluids with regard to the sulfide-forming elements (Cu, Zn, and others) in the ore genesis of the mid-oceanic ridges. The analysis carried out indicates that the role of such fluids is minor in the hydrothermal systems of the mid-oceanic ridges studied thus far.

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THE PROBLEM OF THE SOURCE OF THE METALS IN HYDROTHERMAL MARINE ORE GENESIS REVISITED*

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Discussed in the article are some aspects of the problem of the source of the metals in hydrothermal sedimentary ore formations in connection with critical comments made by D. V. Grichuk and S. G. Krasnov.

The question of the source of the metal occupies an important position in the problem of the genesis of hydrothermal sedimentary metalliferous and ore accumulations in the active regions of the Pacific. The wide discussion this problem has received in the geological literature has not brought researchers to share a common view point concerning the formation of the chemical composition of the marine hydrotherms and the varied mineral deposits formed on discharge.

In recent years the hypothesis of the importance of the extraction of metals from the rocks of the oceanic crust has gained wide popularity. The important influence this process has on changing the composition of seawater as it migrates through basalts is not questioned. But some researchers regard the crustal source as being a universal source, practically denying that magmatic fluids may play a role in submarine hydrothermal ore formation.

In two articles [3, 4] an attempt was made to analyze published data in the fields of geology-tectonics, mineralogy-geochemistry, and isotopic and experimental data concerning the sources of the metals in hydrothermal sedimentary ore genesis. In these articles it was proposed in a qualitative way that the fluid phase of magmatic melts possibly plays an important role in supplying ore components, first and foremost of sulfide-forming metals such as Cu, Zn, Pb, etc.

*Reply to critical comments by D. V. Grichuk and S. G. Krasnov [8].

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This proposition was thoroughly criticized in an article by D. V. Grichuk and S. G. Krasnov, who treat all the observations and distribution patterns for the elements in the solutions and ore deposits in terms of the hypothesis of the hydrothermal leaching of basalts [8].

Without going into all aspects of the problem, let us consider some of the most important points.

According to D. V. Grichuk and S. G. Krasnov, it is only necessary to determine the fraction of magmatic fluids and the ratio with respect to seawater in the circulating hydrothermal system to obtain a theoretical solution to the problem of their role of magmatic fluids in hydrothermal ore formation. It is difficult to disagree with this premise, assuming that the values are sufficiently convincing, trustworthy, and have a reliable factual basis.

Let us consider in some detail the methods and techniques used in their article to estimate the maximum possible fraction of a magmatic component in marine hydrotherms. This is done in two independent ways.

The first way involves comparing global data on the mean annual emanation of volatiles from the mantle and the total flow of water in the hydrothermal systems of the mid-oceanic ridges. The calculation of the total flow of volatiles is based on O. G. Sorokhtin's theoretical model of the evolution of the Earth [7], and the amount of mantle water is calculated from the mean H_2O content in basalt melts [16].

Such a global estimate can hardly be applied to specific ore-forming systems associated with a highly specific stage of development of the magmatic process. The calculations also ignore the pulsed nature of hydrothermal activity, it assumes possible changes in the amount of the fluid phase both in time and in different systems; direct data on the content of the magmatic components in the hydrotherms is not currently available in the literature, chiefly due to methodological difficulties in defining it. We note that the authors themselves quite properly exclude "local variations" in different hydrothermal systems, the degree of which it has not yet proved possible to determine.

The second way used to estimate the maximum possible fraction of magmatic fluids in hydrotherms is based on data on their carbonic acid content. In addition, the authors used CO_2 as a "geochemical measure" to determine the presence of an amount of the magmatic phase in modern hydrotherms on the sea floor.

It is difficult to agree with this premise for the following reasons.

In addition to CO_2 , the gas phase of high-temperature solutions always contains gases such as H_2 , CH_4 , and He of specific isotopic composition, with the only reliable indicator of the presence of a magmatic component in thermal fluids being the ratio of the 3He and 4He , the so-called helium-isotope measure. On the whole, for regions of high tectonomagmatic activity, primarily for the global system of rift zones, a hydrothermal type of thermal waters is characteristic, with the H_2 content as a rule being closely related to the appearance of mantle helium and possibly achieving high values [10].

As for CO_2 , this compound can in no way be considered a "geochemical marker," much less serve as a basis for quantitative calculations since, on the one hand, not all of the CO_2 in hydrothermal exhalations is magmatic, as evidenced by the wide variations in the isotope composition of the carbon, and on the other hand, carbonic acid is consumed as the solutions migrate in wide-spread secondary carbonatizations of the basalts. Carbonates (calcite, more rarely aragonite) are known to frequently fill voids in basalts, as well as form veins of different shapes and sizes and lenticular inclusions. Taking into consideration that in fresh, unaltered basalts CO_2 is either absent or is present in negligibly small quantities (hundredths of a percent), secondary carbonates must form not by mobilizing CO_2 from the host rocks, but from the primary carbon dioxide of deep-seated origin contained in thermal solutions.

The mechanism of hydrothermal carbonate formation has been considered in the most detailed fashion by S. D. Malinin, who shows that at temperatures above 250-300°C carbonates are deposited as a result of a simultaneous fall in pressure and temperature [12].

Thus, the actual amounts of CO_2 that can be determined in hydrotherms under near-surface conditions in no way correspond to the primary contents of carbon-dioxide from depth, and

TABLE 1. Concentrations of Metals in Thermal Solutions from 21°N, East Pacific Rise [19]

Elements	I	II	III	Elements	I	II	III
Fe	135,6	48,6	39,7	Pb	74,4	37,9	49,0
Cu	2,8	0,001	99,9	Ag	4,0	0,1	97,5
Zn	6,8	2,6	61,8	Cd	20,2	1,9	90,6

Note. The values for Fe, Cu, and Zn are given in mg/kg; those for Pb, Ag, and Cd in μ g/kg; I: solution with T = 350-355°C, pH 3.3; II: solution with T = 270-275°C, pH 3.8; III: "losses" of the element in the course of ore deposition, %.

cannot serve as a basis for estimating the fraction of magmatic fluid in the whole.

The minimum fraction of magmatic fluid necessary is also estimated on the basis of indirect evidence, from the calculated distribution coefficients in the "melt-fluid" system relative to granites, and from the composition of gas-condensates of present-day extrusions of the Bol'shoi Tolbachik volcano. Such calculations do not reflect the real amounts of the smallest fraction of fluid of deep-seated origin necessary if only because the magmatic source is not the sole source of the metals, and the contribution of different sources at the present time cannot be determined quantitatively. Estimating the limiting fractions of fluids required to produce the existing concentrations of metals in hydrotherms on the basis of the composition of the gas-condensates of the Bol'shoi Tolbachik Volcano is even less warranted if we consider the significant scatter in the elemental contents in individual samples (Cu varies over three orders of magnitude, Zn by a factor of more than 150, Ag by a factor of two orders of magnitude, etc.) and allow for the fact that the authors specifically stress the order-of-magnitude nature of the calculations for the extraction of metals [2]. The data obtained reflect chiefly the geochemical specifics of the composition of the volatile components.

The facts and concepts outlined above cast doubt on the legitimacy and the proof of one of the most basic conclusions of D. V. Grichuk and S. G. Krasnov that the "maximum possible fraction of magmatic fluid is one or two orders of magnitude lower than the minimum amount necessary to produce the observed metal contents of the hydrotherms of the mid-ocean ridges" [8, p. 130].

We shall briefly consider the geochemical aspect of the problem.

In [4] I discussed some of the features of the chemical composition of sulfide ores that are difficult to explain using only the leaching of basalts. In particular, the absence of a relationship between the metal contents in the basalts of spreading-zones, ocean hydrotherms, and sulfide formations of the oceanic crust. D. V. Grichuk and S. G. Krasnov attempted to refute this approach by comparing the elemental ratios of Cu, Ag, and Pb to Zn, regarding them as "geochemically similar." The comparison was made using the mean geometric values, using the elemental contents of only 3 samples of thermal solutions and 10 samples of sulfide ores [8, Table 2].

First, it is unclear what motivated them to use the mean geometric values in the given case, since the elemental distribution function has not been established, and their normal (Gaussian) distribution, with the calculation of mean arithmetic rather than geometric values, should be regarded as more natural and traditional. If we also consider that an unacceptably small number of samples (3 and 10) was used for the calculations, and that the scatter of the elemental ratios in the sulfide ores varies between factors of 12 and 40 [8, Table 2], then it becomes clear that the numbers obtained are unrepresentative, and thus that the conclusion about the close relationship between the element ratios in basalts, hydrotherms, and sulfide ores of the ocean bottom is only weakly based.

It is also difficult to concur with including Cd, Zn, Pb, and Ag in a group of elements geochemically similar in "migration forms" and in "sulfide-forming ability" [8, p. 124]. These elements have different degrees of affinity for sulfide sulfur, and their chloride complexes, the major form in which they are transported in thermal solutions, are of different stabilities, so that they have different abilities to migrate, leading to their marked separation in the process of ore deposition. Let us illustrate this by comparing the metal contents in two samples of a thermal solution (Table 1).

Judging from the temperature, the pH value, and the element contents, the first sample reflects the composition of a primary hydrothermal solution, and the second sample is to a significant extent a "spent" solution, i.e., one that has lost some of its components in the course of ore deposition.

From the data given in Table 1 it follows that elements like Cu and Ag are extracted from the solutions first and most completely. It is known that phenocrysts and vein mineralization in basalts are characterized by the wide development of Cu sulfides, and in the walls of ore-channels, elevated Ag contents are noted, in particular, the mineral tennantite $(\text{Cu}, \text{Ag})_{10} \cdot (\text{Fe}, \text{Zn}, \text{Cu})_2 \text{As}_4 \text{S}_{12}$ is noted [18].

Of the three most important sulfide-forming elements, the least mobile is copper, and the most mobile is lead; zinc occupies an intermediate position. (The following percentages of the metals were isolated from a thermal solution from 21°N: Cu 99.9, Zn 61.8, Pb 49; cf. Table 1.)

This same pattern was noted by us earlier for ore-formation in the Atlantis II Deep (Red Sea) [6]. For example, in the bottom layer of the brine, the Cu content is about 40 times higher than in ordinary seawater, the Zn content is about 1000 times higher, and the Pb content is about 10,000 times higher. According to figures given in [13], the concentration factors of these same elements in the pore waters of the ore sequence of the Atlantis II Deep exceeded those of seawater by the following factors: for Cu, 107-654; for Zn, 1600-2600; and for Pb, 88,000-199,000.

The copper-rich sulfide accumulations in the Red Sea are rigorously confined to regions of hydrothermal exhalations, and lead minerals as such were not discovered in the sediments [5].

The most probable reason for this pattern is the relative stabilities of the migrating (chiefly chloride) complexes of the elements; it has been established that of the three main chalcophile metals Cu, Zn, and Pb, Cu complexes are the least stable, and Pb the most [17].

Taking the foregoing into account, as well as the exceptionally large scatter in the contents of the metals in the sulfide ores of the ocean floor, the similarity of their ratios in solutions, ore deposits, and tholeiitic basalts should be treated with caution rather than used as an argument for a geochemical relationship between ore formation and the leaching of basalts.

The hypothesis of the recycling and extraction of ore-forming metals from the rocks of the oceanic crust assumes the existence of extensive depletion aureoles in the regions where hydrothermal sedimentary deposits are developed. We note that even proponents of this hypothesis point out the clear discrepancy between the quantity of metals concentrated in the ores, the volumes of basalt required to provide these quantities, and the observed degree of hydrothermal alteration.

For example, in [15] it is computed that for 2 million tons of zinc to accumulate in the sediments of the Atlantis II Deep (Red Sea) from leached basalts containing on the average $100 \cdot 10^{-4}\%$ of this metal, 67 km^3 of rock are required (a 1-km-thick body $15 \times 4.5 \text{ km}$), it being assumed that $\sim 10\%$ of the Zn is dispersed to neighboring areas. In the same article the opinion is expressed that the ore deposits of the East Pacific Rise require the leaching of substantially larger volumes of basalts, since quite significant amounts of the metals are dispersed over comparatively wide areas, and some remain in the basalts, forming secondary stockwork-type mineralization.

The hypothesis of the hydrothermal leaching of basalts as the sole source of the metals in the ore-forming process also contradicts some geochemical data obtained in a study of hydrothermally altered seafloor.

For example, according to calculations presented in [11], based chiefly on deep-water drilling data, every year as a result of hydrothermal action the following amounts of metals (in millions of tons) are extracted from the basalts of the mid-ocean ridges and seamounts: Fe 117.5; Mn 4.85; Ni 0.9; Zn 0.47, Cu 0.29; Co 0.17; i.e., approximately twice as much nickel is extracted as zinc, and three times as much nickel as copper. Without going into the reliability of these estimates we note that if only the crustal source were responsible for supplying the metals, then considering the affinity of Ni for sulfide sulfur one would expect to find high concentrations of it in ocean-bottom sulfide ores, or accumulations of Ni in secondary minerals of the formations of the basaltic basement. Nevertheless, the facts

indicate exceptionally low values of Ni in ocean-bottom sulfide-ores - the massive sulfides of 21°N, East Pacific Rise and the Juan de Fuca Ridge contain, in %: Ni $2 \cdot 8 \cdot 10^{-4}$, Cu up to 10, and Zn up to 60. Nor are nickel-enriched products of hydrothermal activity noted in the oceanic basalts column [11]. The geochemical features of the sulfide formation of the oceanic crust are more easily classified as evidence for the active involvement of magmatic fluids in hydrothermal ore formation and on the whole, are in agreement with the mobility (volatility) of the metals on their removal from the melt [2, 4].

As for the heat balance of hydrothermal systems, it is important to consider data published in a recent Benchmark volume edited by P. Rona analyzing hydrothermal processes occurring at seafloor spreading centers [14]. Here it is stressed that in the spreading centers of the Pacific, hydrothermal convection occurs almost everywhere, while ore-forming systems are developed only locally, under conditions of anomalously high temperature gradients that differ sharply from the background level and that require an additional source of heat.

We point out that V. I. Kononov has also demonstrated by appropriate calculations the necessity of an additional (to the convective) source of heat in the largest hydrothermal systems, the most probable form for this source being assumed to be the entry of high-temperature gas-rich fluids [10]. The possibility is also noted of an indirect intrusion of magmatic melt into the hydrothermal system, which has been demonstrated in the Krabla deposit in the Central Nonvolcanic Belt in Iceland, the landward extension of the rift zone of the Mid-Atlantic ridge.

The most probable heat and mass vehicles are intermediate magma chambers, with which hydrothermal activity has been convincingly shown to be associated, including in the Red Sea [1].

In conclusion, we note that an analysis of the factors and hypotheses concerning the sources in hydrothermal sedimentary oceanic ore genesis gives grounds for assuming that most of the components of the hydrotherms are polygenetic, it being unfortunately necessary to add that the present state of our knowledge does not allow us to reliably estimate numerically the contribution or relative involvement of genetically different components in the process.

It is all the more important to take an all-inclusive approach to the study of this problem, to consider alternative points of view to new factual information, that eventually will bring us to understand the true natural relationships.

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UTILIZING THERMAL ANALYSIS IN THE STUDY OF DOLOMITES OF
DIFFERENT ORIGINS (BEREZOVIAN FOREDEEP, SIBERIAN PLATFORM)

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UDC 552.543:552.08

The development of reliable criteria for distinguishing between primary (sedimentary) and epigenetic dolomites is of practical as well as theoretical importance. This practical importance is associated with the wide-scale development of epigenetic dolomitization in the ore fields of stratiform lead-zinc deposits, which may serve as one of their predictive criteria [1, 2, 5].

The region-wide development of epigenetic dolomitization has been established by the authors in the eastern part of the Pribaikal-Charskian zone, where stratiform bodies of dolomitized metasomites (dolomites) are distributed throughout the unmetamorphosed terrigenous-

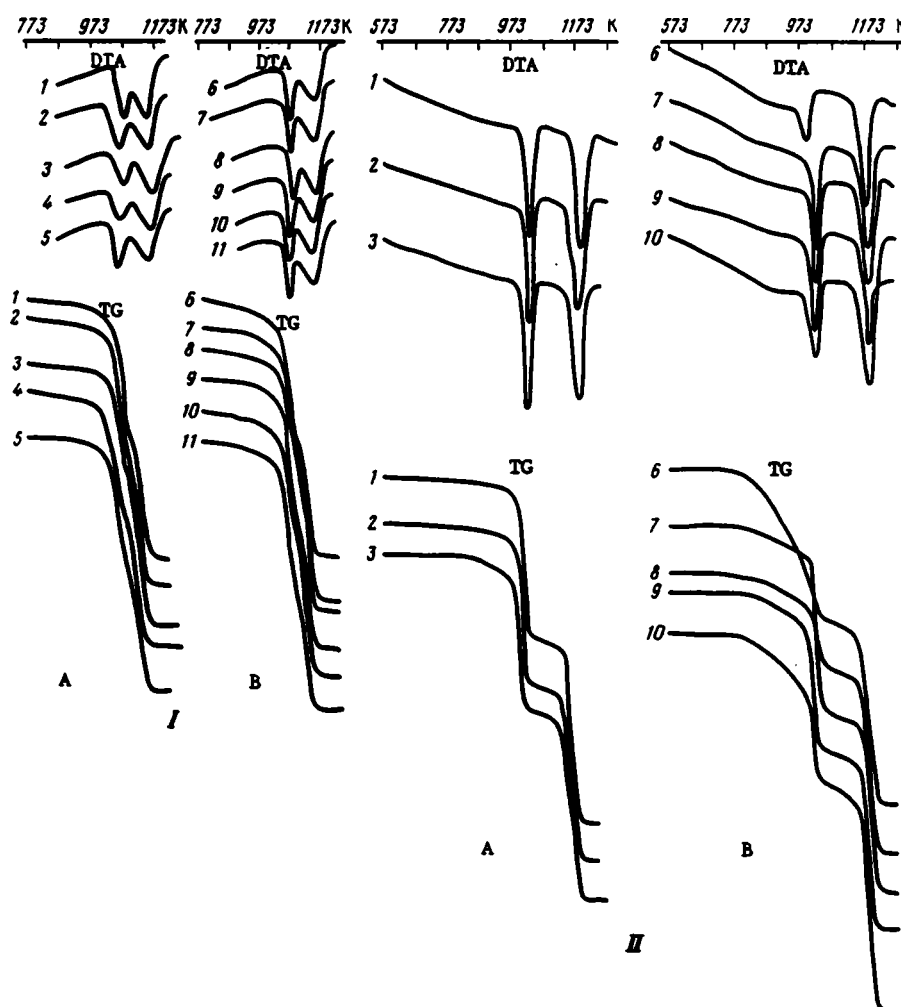


Fig. 1. Thermal analysis curves of sedimentary (A) and metasomatic (B) dolomites: I) nitrogen atmosphere; II) sealed sample-holders (atmosphere of evolved CO_2).

carbonate deposits of the Berezovian pericratonic foredeep (Fig. 1). There hydrothermal metasomatic formations were previously classed [3] as carbonate metasomatites of the basified series (in the terminology of [4]).

Geological mapping showed that dolomitization was accompanied by calcification and baritization of the host rocks. The end products (inner belt) of dolomitization are the anchi-minomineralic "sugary" dolomites that determine the composition and name of the formation. In the outer alteration zones (the aureole), dolomitization and porphyroblastic baritization appear.

The dolomitic metasomites form from the limestones of the Torginskian Formation of the Late Riphean and to some extent from the sedimentary dolomites of the Sen'skian Formation. The micaceous-calcitic metasomites that are associated with the dolomites and that form the upper part of the vertical metasomatic column are developed in the overlying Vendian sandstones of the Zherbin Formation. Baritization is more characteristic in the terrigenous-carbonate rocks of the Sen' Formation. The area over which the altered rocks extend is delimited by regional long-lived faults trending northeast-southwest and nearly north-south. Local low-lying faults control the position of the individual bodies of completely exposed metasomites.

The dolomites and dolomitized limestones contain as secondary and accessory minerals the following: calcite, chlorite, apatite, fluorite, barite, galena, cleiophane [var. sphaerite] of a number of generations, and pyrite (marcasite). This last is sometimes found in significant quantities. The dolomite metasomites are distinguished from the host rock limestone by their variegated colors, their distinct crystallization, and their massive and brecciated appearance. The thickness of individual bodies reaches 50-70 m and they extend for 2-3 km. The age of the dolomites of the Berzovian foredeep was established as Mesozoic (about 190 million years) on the basis of geochemical data confirmed by isotopic dating (L. I. Kalinicheva, VSEGEI).

With the aim of determining the specifics of the composition of the dolomitic metasomites and of comparing them with dolomites of the Sen'skian Formation, reliably known to be of sedimentary origin, we studied their chemistry and did thermal and x-ray studies on them. In comparing the data obtained by these analyses it was found that both genetic rock types consist chiefly of dolomite, with the sedimentary formations having a more uniform composition. The metasomatized dolomites contain significant amounts (up to 50%) of calcite, pyrite, barite, and are distinguished by somewhat higher concentrations of iron and manganese (Table 1), which defines the nature of the petrogenetic process.

The powder patterns of the sedimentary and the epigenetic dolomites are practically identical. Calculating the values of the unit cell values, we note only a very slight tendency for the c value of the dolomites of hydrothermal metasomatic origin to be larger (cf. Table 1).

The most informative technique for determining the differences between the dolomites of different origins proved to be thermal analysis. The DTA and TG curves recorded on high-speed thermal-analysis systems (TU-1M, UTA-1) and with a MOM derivatograph (Hungary) do not show any differences between the two dolomites of different origins; a difference in their thermal behavior was detected only when we compared their DTA curves taken under a flow of inert gas and in sealed crucibles (Fig. 2).

It is known [8] that the two-step thermal decomposition of dolomite involves the decomposition of the dolomite in the first step to form MgO and CaO , with the simultaneous recarbonation of the latter to $CaCO_3$, and the decomposition of the newly-formed calcite in the second step. The atmosphere in which the decomposition occurs, or more precisely, the CO_2 partial pressure in the system as it heats, has little effect on the temperature of the first endotherm, but a substantial effect on the temperature of the second, raising the t_{max} of the endotherm from $650^\circ C$ (under vacuum) to $950^\circ C$ at $p_{CO_2} = 1$ atm. Accordingly, the appearance of the DTA curves for dolomite also changes markedly as the CO_2 partial pressure changes. We therefore compared the DTA curves of the two types of rocks being studied, after these were recorded both under an inert gas, nitrogen, (in cone-shaped corundum sample-holders) and in sealed sample-holders, i.e., in an atmosphere of the CO_2 liberated in the process. The first case provides an opportunity to study the intermediate products of the decomposition of the dolomite, since the nitrogen atmosphere rules out the possibility of the metal oxides recarbonizing, and in addition, when the gaseous decomposition products are constantly removed,

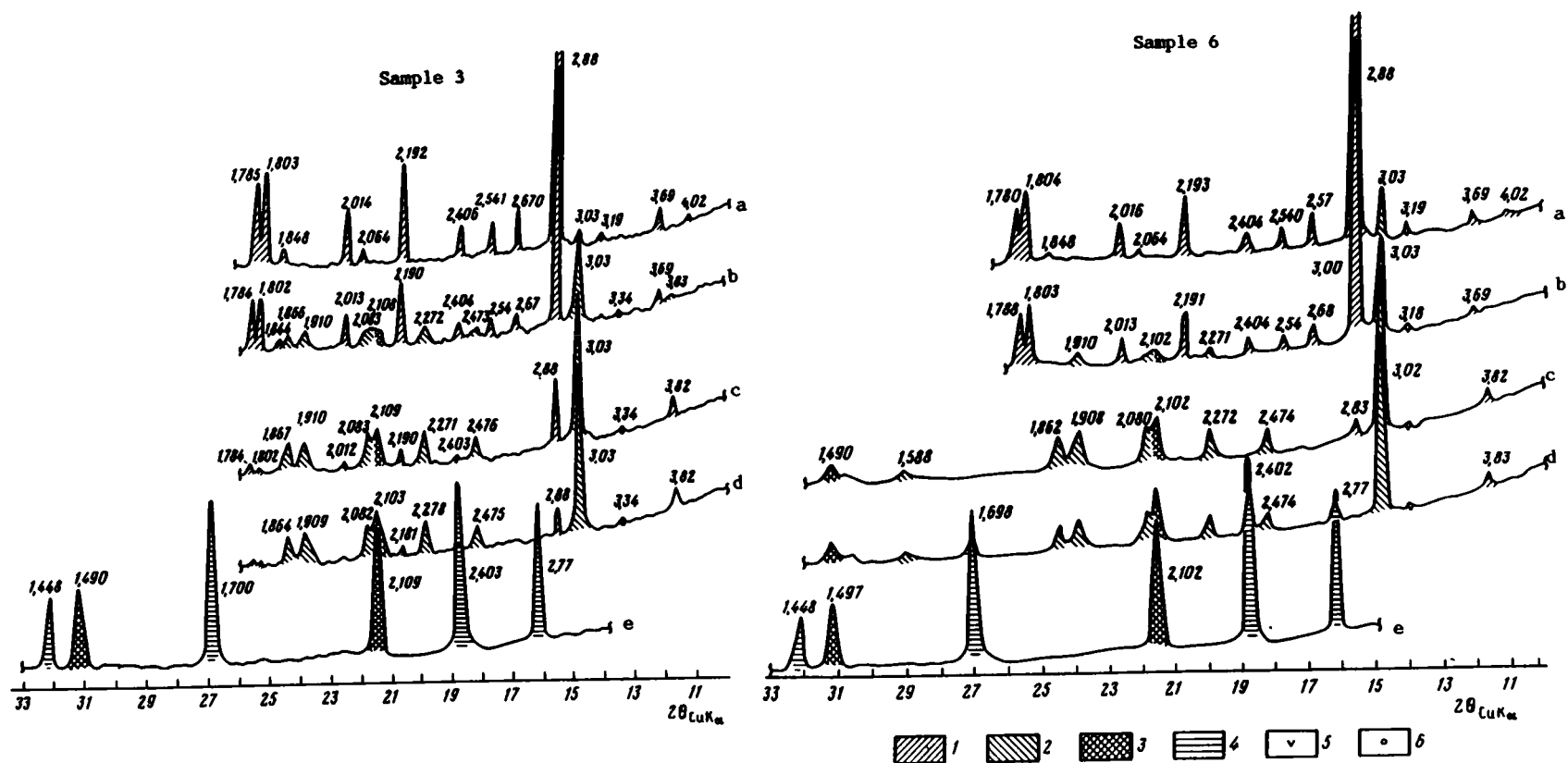


Fig. 2. Powder diffraction curves of a sedimentary (sample 3) and a metasomatic (sample 6) dolomite and the products formed by heating them. 1) Dolomite; 2) calcite; 3) MgO; 4) CaO; 5) feldspar; 6) quartz; a) original sample; b-e) samples calcined to, respectively, 760, 780, 810, and 960°C.

TABLE 1. Results of the Chemical and X-Ray Diffraction Analyses of Sedimentary and Metasomatic Dolomites

Sample number	Cell constants (numerator: a; denominator: c)	Content, %												
		SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	S	calcin. loss	Total
Sedimentary dolomites														
10540	<u>4,807</u> 16,012	0,2	0,03	0,1	0,1	0,03	0,03	17,35	35,74	0,02	0,06	0,02	45,66	99,19
10602	<u>4,807</u> 16,010	1,59	0,06	0,57	0,23	0,22	0,02	18,97	32,33	0,1	0,3	Not det'd	45,92	100,06
10600	<u>4,808</u> 16,012	0,51	0,3	0,1	0,13	0,05	0,05	20,08	33,22	0,03	0,06	"	45,95	100,17
Metasomatic dolomites														
10499-3	<u>4,809</u> 16,021	0,89	0,03	0,1	0,87	0,86	0,19	17,42	33,81	0,04	0,02	0,04	46,55	99,84
1058	<u>4,808</u> 16,018	Not determined												
1105-a	<u>4,810</u> 16,011													
10531-4	<u>4,812</u> 16,014	0,32	0,03	0,15	0,29	0,9	0,04	18,81	33,62	0,04	0,13	0,02	46,47	100,01
10497	<u>4,811</u> 16,021	1,29	0,04	0,2	0,9	0,83	0,07	17,94	33,34	0,02	0,12	0,02	46,47	100,59

*CO₂ is included in "calcination loss"; P was not determined.

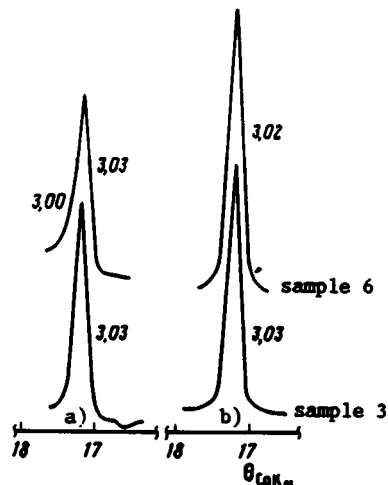


Fig. 3. Sections of the DTA curves for the heating products of a sedimentary (sample 3) and a metasomatic (sample 6) dolomite. a) Up to 760; b) up to 780°C.

the specific features of the decomposition of the dolomites associated with defects in their crystal structure become more visible. Recording the DTA curves in sealed crucibles provides for a maximally saturated CO_2 atmosphere, and a clear-cut differentiation of the endotherms on the DTA curves (the decomposition temperature of CaCO_3 is significantly raised) and the steps in weight loss on the TG curves are observed.

In terms of the nature of their thermal decomposition (their DTA and TG curves)* the two dolomites can be clearly divided into two groups (with the members of each group being similar to each other), the two groups corresponding to the dolomites of sedimentary and metasomatic origin (cf. Fig. 2).

In order to understand the differences in the nature of the thermal decompositions of the metasomatic and the sedimentary dolomites, we selected typical representatives of each group and subjected them to thermal/x-ray investigation: the samples were heated successively to 760, 780, and 810°C, cooled in a flow of nitrogen to room temperature, and immediately subjected to x-ray analysis.

As can be seen from Fig. 3, the difference in the mechanism of the decomposition of the dolomites of the two different groups is due to the formation of an intermediate product in the metasomatic dolomite with d values of 3.00 and 3.02 Å in addition to pure calcite with $d = 3.03$ Å; this corresponds to an isomorphous replacement in the calcite by 12 and 5 mole % MgCO_3 [9]. At 780°C, only a phase with $d = 3.02$ Å forms. This is evidence that the decomposition mechanism of the metasomatic dolomites differs from the theoretical reactions



and follows the scheme



When the curves are recorded for sealed sample-holders, i.e., in an atmosphere of the CO_2 liberated, due to the increase in the temperature of the decomposition of the calcite formed as an intermediate product of the decomposition of dolomite according to reaction (1), the first and second endothermic effects (temperature interval approximately 160°C) become clearly differentiated. At the same time, the DTA curve of the metasomatic dolomites (cf. Fig. 2) shows an additional (compared to the DTA curves of the sedimentary dolomites) very weak and ill-defined endothermic effect with a maximum at $t \sim 600^\circ\text{C}$; to this hardly noticeable

*The same conditions were used for recording the DTA curves for all the samples: atmosphere) N_2 flow; N_2 flowrate) 40 liters/h; exhaustion rate) 10 liter/h; sample-holders) conical corundum; sample weight) 200 mg; sensitivity for TG) 100 mg, for DTA) 1/5, for DTG) 1/10; heating rate) 10°C/min; chart rate) 2 mm/min.

endotherm on the DTA curve there corresponds a quite marked weight loss on the TG curve. Thus, the differences in the nature of the thermal decomposition of metasomatic and sedimentary dolomites show up most clearly in the TG curves. For the metasomatic dolomites, weight loss begins approximately 100°C earlier than for the sedimentary dolomites, and at the moment when the main mass of the dolomite begins to decompose (i.e., at 750-800°C), from 9.5 to 20% of the total CO₂ is liberated, while in the sedimentary dolomites this value varies from 3.3 to 3.9%.

The differences discovered in the mechanism of the thermal decomposition of the two types of dolomite being studied suggests that they reflect structural differences. It is possible that the structure of the metasomatic dolomites contains defective regions which undergo thermal decomposition significantly more readily, i.e., at a lower temperature, than the main body of the crystals. These disturbances may be due to different reasons, in particular, cation disordering, a result of their being formed by the Mg-metasomatism of calcite. In any case, however, the specifics of the thermal behavior of the metasomatic dolomites we have found are governed by the conditions under which they formed and may serve as reliable criteria for distinguishing them from dolomites of other origins, in agreement with earlier conclusions [6].

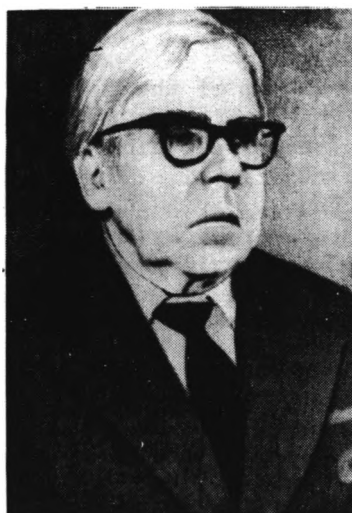
The fact that it is possible to identify the metasomatic (epigenetic) dolomites that in ore fields often accompany stratiform lead-zinc deposits localized in carbonate rocks and polymetallic metallization using thermal analysis may be of great importance in the early stages of exploration in predicting the mineralization.

Thus, a new dolomite hydrothermal-metasomatic formation has been identified in the territory of the Berezovian Foredeep of the Siberian Platform. Shows of galena-siderite mineralization established in the dolomites and dolomitized limestones of the Berezovian Foredeep improve the changes that this territory contains polymetallic mineralization, considering its proximity to known lead-zinc mineralization in the jasperoids of the Dzhelindinsk ore cluster [7].

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ALEXANDR VASIL'EVICH KHABAKOV



Soviet geological science has suffered a major loss: on January 12, 1988, at the age of 84, the prominent Soviet geologist, Doctor of Geological and Mineralogical Sciences Alexandr Vasil'evich Khabakov died.

A. V. Khabakov's scientific activity was tied to the All-Union Scientific-Research Institute of Geology (VSEGEI), where he worked for more than 60 years. There he established and headed, for a very long time, the department of Lithology and Environmental Analysis.

A. V. Khabakov was born August 10, 1904, in Kirillov, Vologda region. In 1925 he graduated from the Leningrad State University, the faculty of Geology and Geography. His first scientific work was published in 1924. Without defending the dissertation he was awarded both scientific degrees: in 1940 – candidate, and in 1964 – doctor of Geological and Mineralogical Sciences. A. V. Khabakov always paid close attention to field investigation. For 32 years (from 1921-1953) he annually participated or headed the field works at such difficult places as: the Arctic, Ural coniferous forest, and Pamirs.

Field work was very important for A. V. Khabakov with relation to the structure and genesis of different deposits of mineral resources.

He authored the geological maps of the southern part of the Vyatka-Kama phosphorite basin, the Orsk-Khalilovo copper-nickel, chromite, and iron-ore deposits, the Blyava pyrite deposit, the Dombarovsk coal and kaolin deposits, the Kirov asphalt deposits, the Inder potassium and borate deposits, and also he discovered the lapis lazuli deposit in the source of the river Lyadzhvar-Dar in Pamirs.

Many times, as a high level specialist, A. V. Khabakov inspected the phosphorite mines of the Ukraine Podoliya, Kirov region, the mine Sol'-Iletsk in the South Ural, and others. He consulted on the construction of railroads, including: Pinyug-Ust'-Sysol'sk and Budugoshch'-Krasnyi Kholm.

During World War II, A. V. Khabakov worked for the Committee of Geology of the Soviet Council of People's Commissars. He oversaw appraisal of the South Ural deposits, and personally investigated a few ore mines, including Magnitogorsk, Dzhezdy, and others.

Translated from *Litologiya i Poleznye Iskopaemye*, No. 1, pp. 142-143, January-February, 1989.

After World War II, A. V. Khabakov came back to the VSEGEI and began to study conditions of the conglomerate rock formations at the West Ural, Pai-Khoi, and Sibiria, where he found very valuable information about the structural relations of these regions.

From 1945-1949, A. V. Khabakov lectured on paleogeography at the Leningrad State University.

As a highly educated person, A. V. Khabakov had a deep knowledge in sciences other than geology, such as: chemistry, mathematics, and astronomy. Lunar science held a special place in his scientific work. He was one of the first who tried using geological methods to define the main stages of lunar surface development. Khabakov's monograph: On the Main Principles of the History of Lunar Surface Development, published in 1949, is widely known and has become a classic work on lunar geology. Later, he published five more works devoted to the geological formation of the moon.

A. V. Khabakov's comprehensiveness was remarkable: lithology, environmental analysis and paleogeography, regional geology and geological cartography, cosmic geology, and history of science.

Suffice it to say that most of Khabakov's works were pioneering, and they were further developed by his followers later on.

A. V. Khabakov's works in the paleogeography of fragmented rocks and the particular article: "Dynamic Paleogeography, its goals, and applications" encouraged the propagation of paleogeographic investigations in the USSR. He initiated and edited the unique work: "The Atlas of the Lithological and Paleogeographical Maps of the USSR." A. V. Khabakov pioneered the study of radiolaria in the USSR, and was one of the founders of the method for finding the paleotemperature of carbonate rock formation.

A. V. Khabakov was a devotee of native geology. His paper: "Essay in History of the Knowledge of Geological Exploration in Russia," and a range of works helped to cast light on many hitherto unknown aspects of the activities of M. V. Lomonosov and other early Russian scientists. A. V. Khabakov's contribution in development of the Soviet regional geology was very valuable, especially his investigation of the Ural fold area.

His works: "The Polar Ural and Its Relation with the Other Fold Areas in Arctic Regions" and "Geological Formation of the Kara Sea Coast of the East Pai-Khoi" laid foundation of the modern understanding of geological formation of this difficult terrain and little known part of the Ural.

It was typical for all A. V. Khabakov's creative activities to combine theoretical, practical, and methodical approaches as well as detailing with wide fundamental generalization.

Khabakov authored over 150 scientific works. All his works were distinguished by excellent writing, originality of ideas, and were conclusive.

For his long scientific life and fruitful activities, A. V. Khabakov was awarded the Order of Lenin, the Order of the Labor Red Banner, and many medals.

The bright memory of Alexandr Vasil'evich Khabakov - prominent, original, and comprehensive scientist - will remain forever with his co-workers, students, and many followers.

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